Zeolite Membrane Reactor for Pre-Combustion Carbon Dioxide Capture

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DOE Award:

DE-FE0026435

Budget Period 1 Review Meeting

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Pittsburgh, Penn

Outline

Introduction

BP1 Progress and Accomplishments

- ❑ Experimental Study on WGS in Lab-Scale Tubule Zeolite Membrane Reactor (Task 2.0)
- ❑ Modeling and Analysis for WGS in Zeolite Tubule Membrane Reactor (Task 3.0)
- ❑ Optimizing Tubule Support Fabrication (Task 4.0)
- ❑ Optimizing Zeolite Membrane Synthesis Methods (Task 5.0)
- ❑ Scaling up Synthesis of High Quality Zeolite Membranes (Task 6.0)
- ❑ Design and Fabrication of Zeolite Membrane Bundles and Modules (Task 7.0)
- ❑ Testing Zeolite Tube Bundles under Gasifier Conditions Including Membrane Reactor Configuration (Task 8.0)
- ❑ Establishing Conceptual Process Design, Performance Model and Preliminary Techno-Economic Analysis of WGS Zeolite Membrane Reactor Technology (Task 9.0)

Summary of Accomplishments, Training and Professional Development

Expenses for Budget Period 1 and Budget for Budget Period 2

Plan for Current Quarter Work

Plan for BP2 Work

- ❑ Discussion on BP2 Work
- ❑ Tasks and Timeline of BP2

Introduction

Overview

Timeline

- Project start date:
  Oct.1, 2015
- Project end date:
  Dec.31, 2018
- Budget Periods:
  I: 10/1/2015-6/30/2017
  II: 7/1/2017-12/31/2018

Research Area

2B2: Bench-Scale Pre-Combustion CO_2 Capture Development and Testing

Budget

- Total project funding
  - DOE **$2,471,557**
  - Cost-share: **$620,527**
  - Total**: $ 3,092,084**
- Funding for BP I:
  - DOE **$1,274,869**

Partners

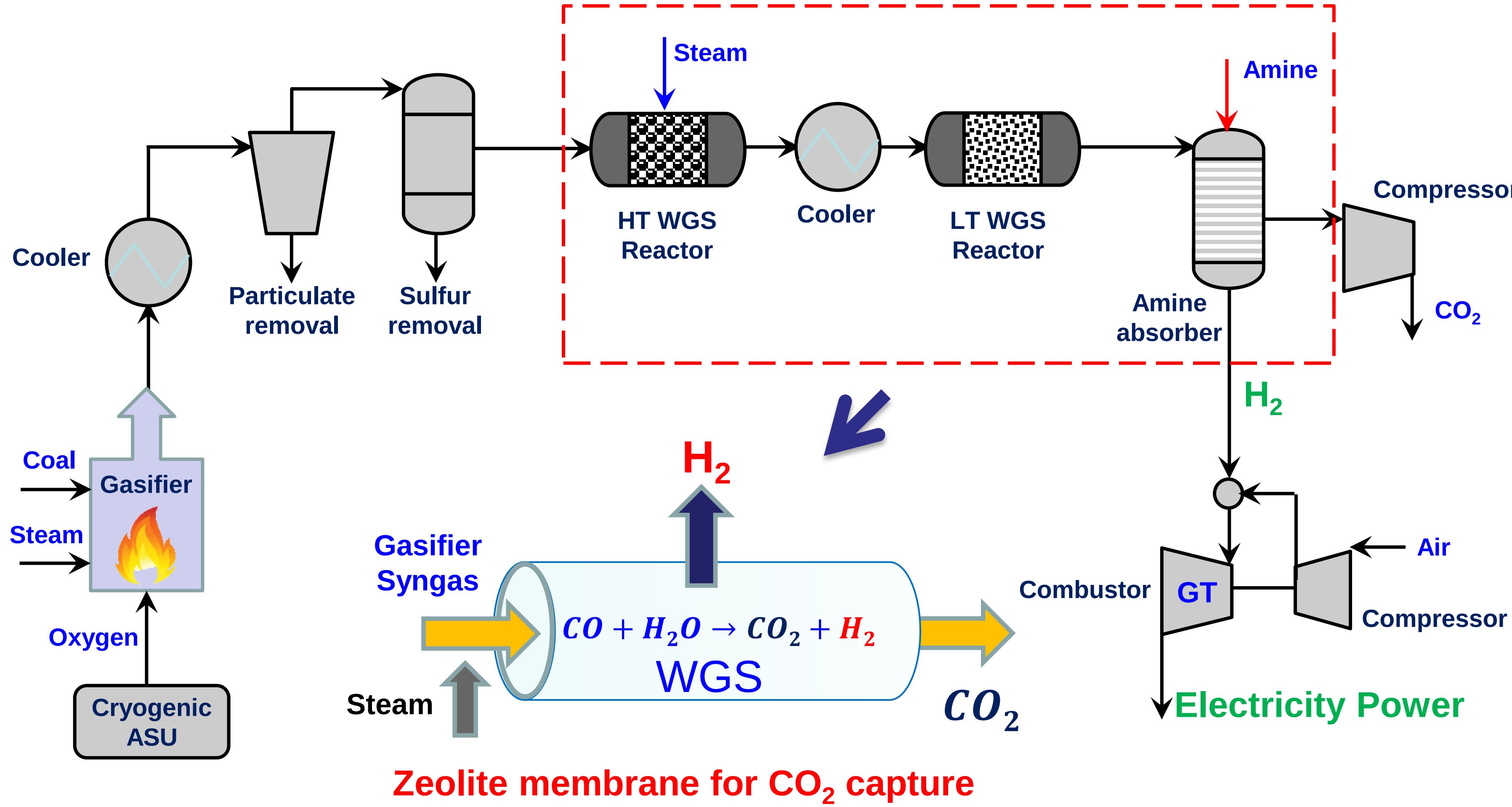
- Arizona State University (ASU)
- University of Cincinnati (UC)
- Media and Process Technology, Inc (MPT)
- Nexant, Inc.

Project Objectives

To demonstrate a bench-scale zeolite membrane reactor for WGS reaction of coal gasification gas for hydrogen production for integration with IGCC power plant.

To evaluate the performance and cost-effectiveness of this new membrane reactor process for use in 550 MW coal-burning IGCC plant with CO_2 capture.

Zeolite Membrane Reactor for Water-Gas Shift Reaction for CO_2 Capture

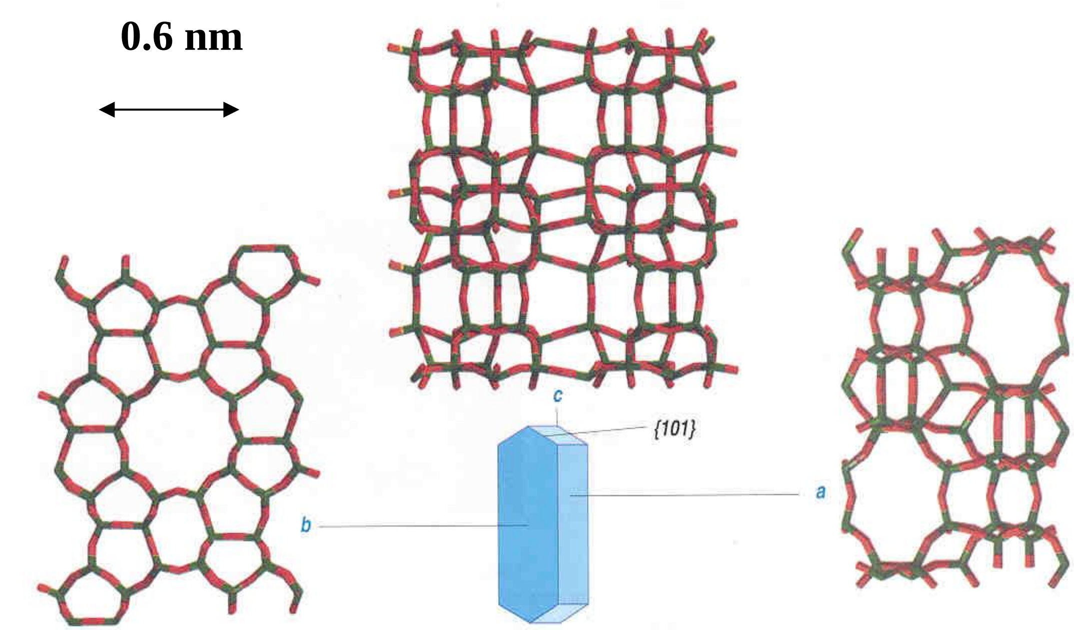


Zeolite Membrane Requirements:

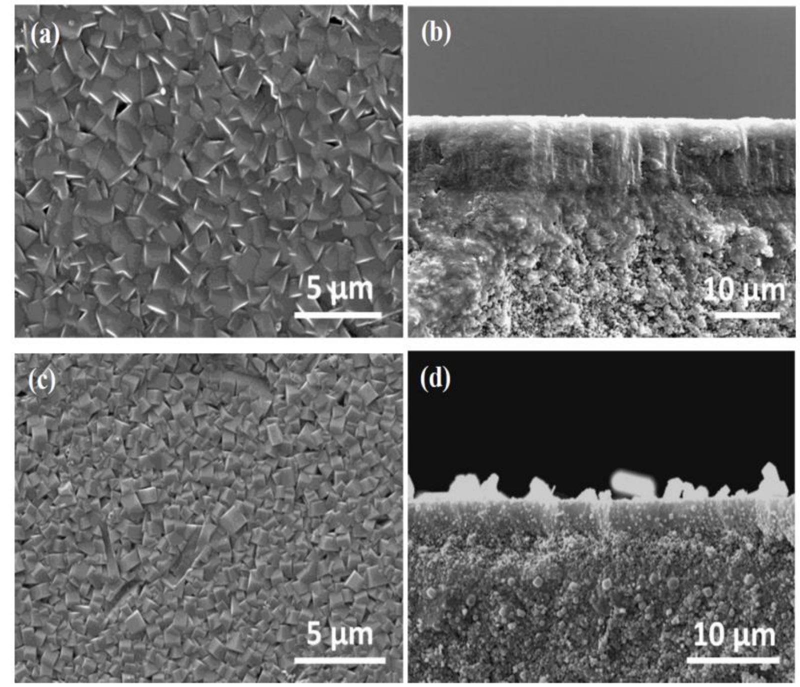
- Operate at 350-550°C
- Chemically stable in H_2S, thermally stable at ~400°C
- Hydrogen permeance > 1×10^{-7} mol/m^2.s.Pa (>300 GPU)
- Hydrogen selectivity >25

MFI Type Zeolite

Structure of MFI type Zeolite (ZSM-5 or Silicalite)



Highly chemically and thermally stable (up to 700^{o}C)



Surface and cross-section SEM images of (a, b) templated synthesized random oriented MFI membrane, (c, d) template-free synthesized random oriented MFI membranes (from Lin lab)

Properties of Lab-Scale CVD Modified MFI Zeolite Membranes (Disk Shape)

Parameter	Value
H_2 Permeance in ($mol/m^2.s.Pa$)	$1\text{-}4 \times 10^{-7}$
H_2 Permeance in GPU	300-1200
H_2/CO_2 selectivity	20-140
H_2/CO selectivity	50-200
H_2/H_2O selectivity	120-180
H_2/H_2S selectivity	100-180
Tested stability hours in syngas stream at 400 ppm H_2S at 500^oC	600

With equal-molar feed of H_2, CO_2, CO and H_2O at 500^oC and 2 bar feed (Lin and Dong Labs)

Scope of work

1) **Scaling up a zeolite membrane reactor from lab-scale to bench-scale for combined WGS reaction and H_2 separation**
2) **Conducting a bench-scale study using this zeolite membrane reactor for hydrogen production for IGCC with CO_2 capture.**

Goal is to demonstrate effective production of H_2 and CO_2 capture by the bench-scale zeolite membrane reactor from a coal gasification syngas at temperatures of 400-550°C and pressures of 20-30 atm:

- Bench-scale zeolite membrane reactor: 21 zeolite membrane tubes of 3.5 ID, 5.7 OD and 25 cm L(active)
- A system producing H_2 at rate of about 1-10 kg/day, equivalent to a 1-10 kW_{th} IGCC power plant

General Approach to Scaling up WGS Zeolite Membrane Reactor

Single-tube zeolite membrane reactor: study WGS up to 30 atm by experiments and modeling

Intermediate-scale membrane reactor: 7 tube membrane module, and WGS reaction in the intermediate-scale reactor

Bench-scale membrane reactor: 21 tube membrane module, and WGS reaction in the bench-scale membrane reactor at NCCC

Membrane reactor in IGCC with CO_2 capture - process design and techno-economic analysis

BP1 Progress and Accomplishments

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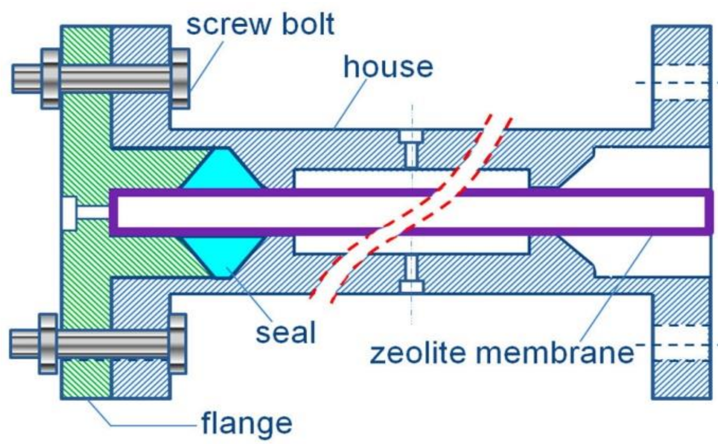
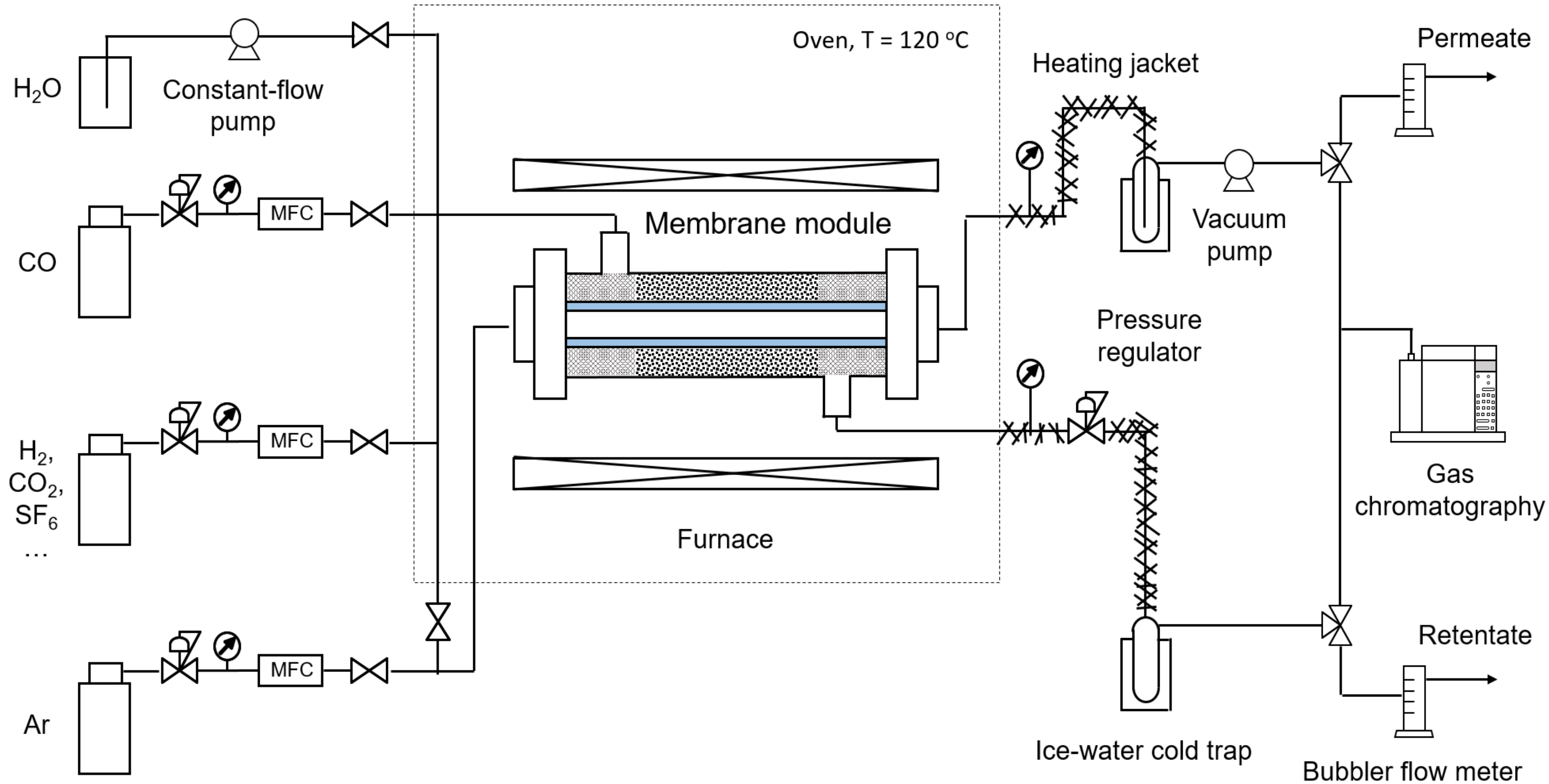
Experimental Study on WGS in Lab-Scale Tubule Zeolite Membrane Reactor (Task 2.0)

Subtask 2.1 Setting up high pressure WGS membrane reactor:

Two single-tube zeolite membrane reactor systems were built (400-550^{o}C, 30 bar), and used to study WGS reaction.





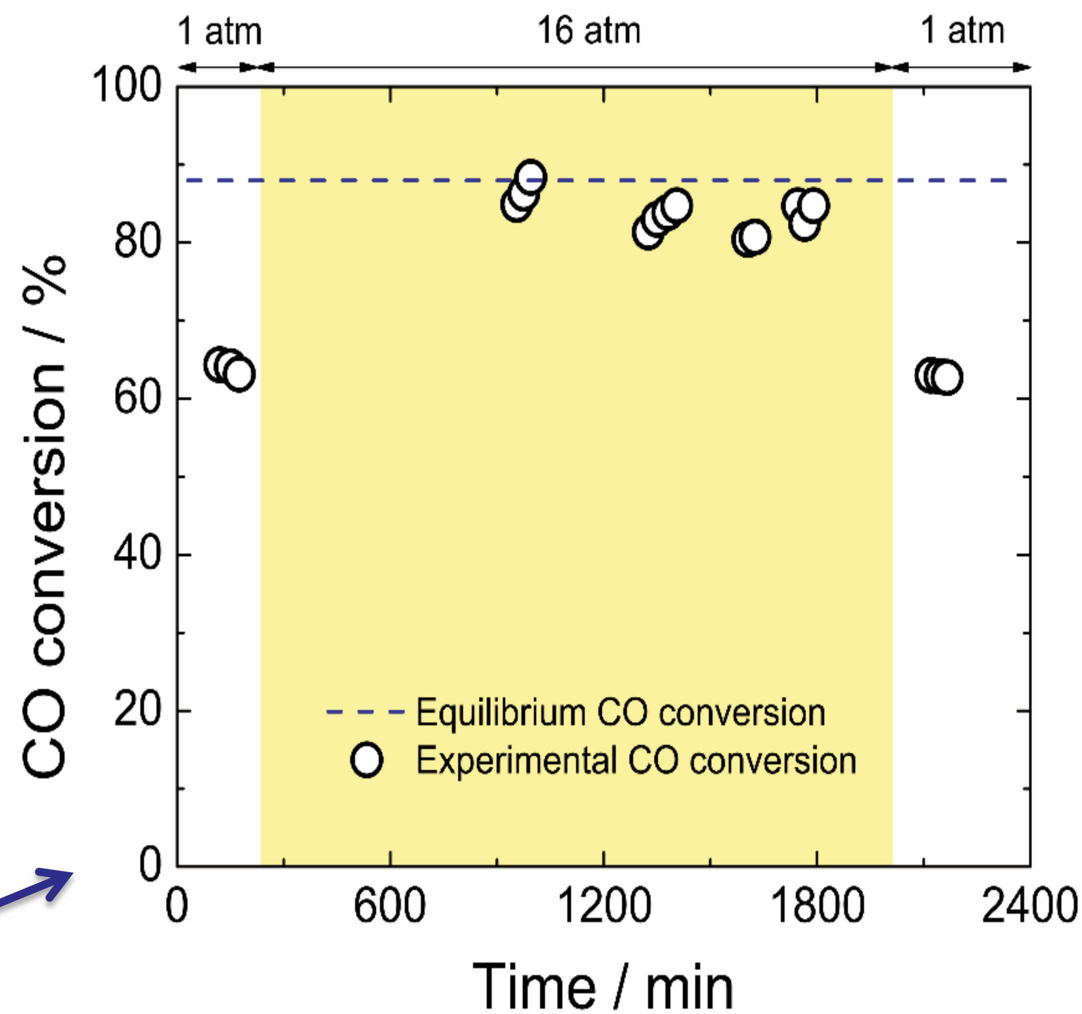
Setup at ASU

Experimental Study on WGS in Lab-Scale Tubule Zeolite Membrane Reactor (Task 2.0) (Cont'd)

Subtask 2.2 Evaluating Performance of WGS catalyst

High temp. Fe/Cr/Ce oxide (10:1:1) as well as Cu doped one were prepared by co-precipitation method

CO conversion in a fixed-bed reactor kept at 550 °C and H_2O/CO ratio is 3, (GHSV) of 24,000 h^{-1}



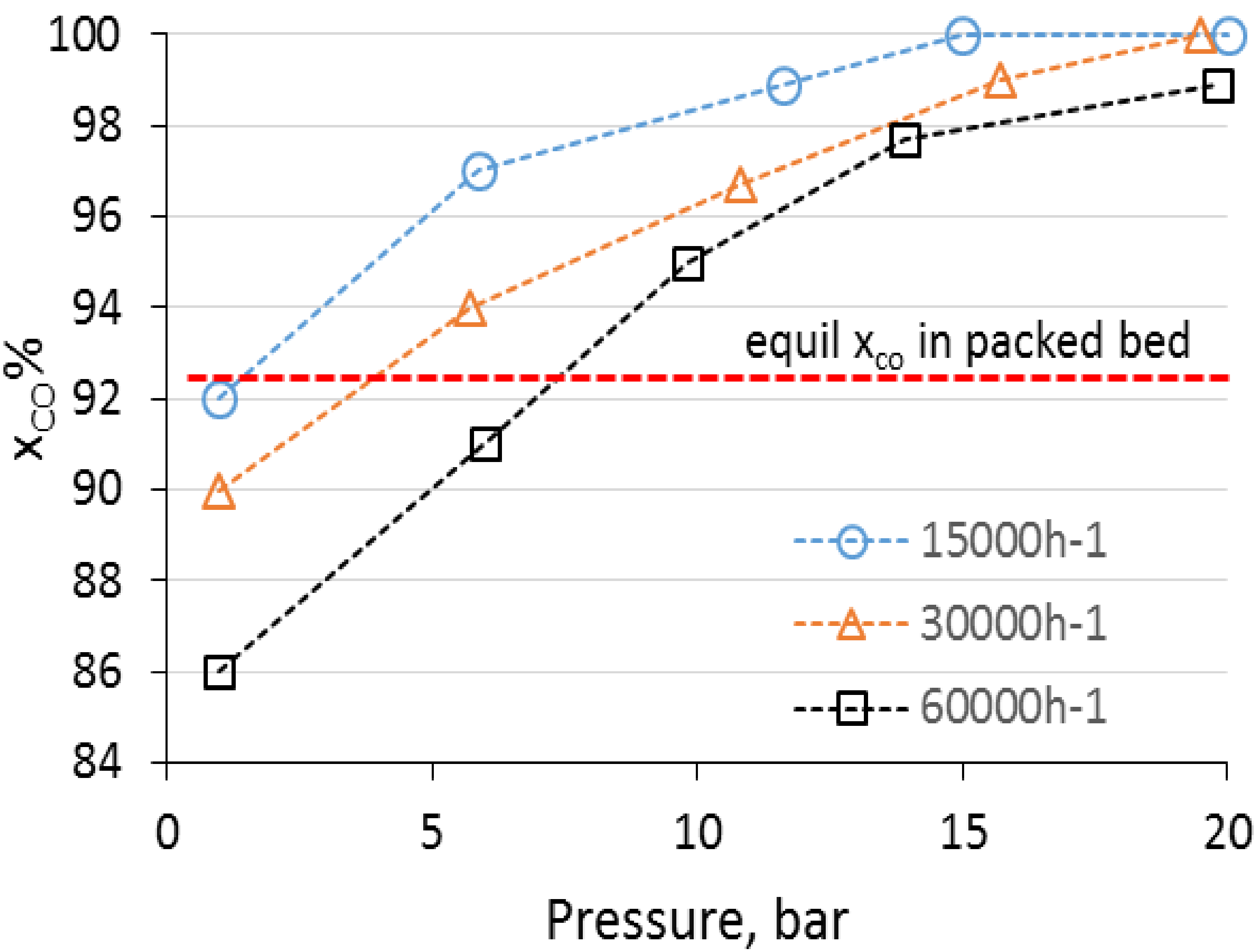
Experimental Study on WGS in Lab-Scale Tubule Zeolite Membrane Reactor (Task 2.0) (Cont'd)

Operation Conditions of Sulfur-Resistant WGS Catalysts

Catalyst	Source	Com-position	Size / mm	Typical testing condition	References
SSK-10	Haldor Topsoe	Co-Mo/ Carrier	5	T = 200-500 °C, Pressure = 20 bar, H_2O/CO = 1.5-2.3, H_2S = 81 ppmv	• Ube Ammonia Co., *Japan*, 1000 MTPD Ammonia • Perdaman, *Australia*, 3700 MTPD Ammonia • POSCO, *South Korea*, 500,000 MTPY SNG • Piteå, *Sweden*, 5 MTPD Bio-DME • IGCC plant, *US*, non-disclosed
Katalco® K8-11	Johnson Matthey	Co-Mo	4	T =230-450 °C, Pressure = 11-12 bar, H_2O/CO = 0.8-6.2, H_2S =274-476 ppmv	• Southern Company Services, *US*, DE-FC21-90MC25140
ShiftMax® 820S	Clariant	Co-Mo/ Carrier	5	T > 250 °C, Pressure = 35 bar, H_2O/CO = 1.26, H_2S > 100 ppmv	• Huayi Energy Chemical, *China*, SGS unit • RTI International, *US*, DE-NT0006479

Experimental Study on WGS in Lab-Scale Tubule Zeolite Membrane Reactor (Task 2.0) (Cont'd)

Subtask 2.3 Experiments on WGS in lab-scale zeolite membrane reactor



Zeolite membrane:

- (α_{H_2/CO_2}) = 38,
- F_{H2} =300 GPU
- Length=8cm

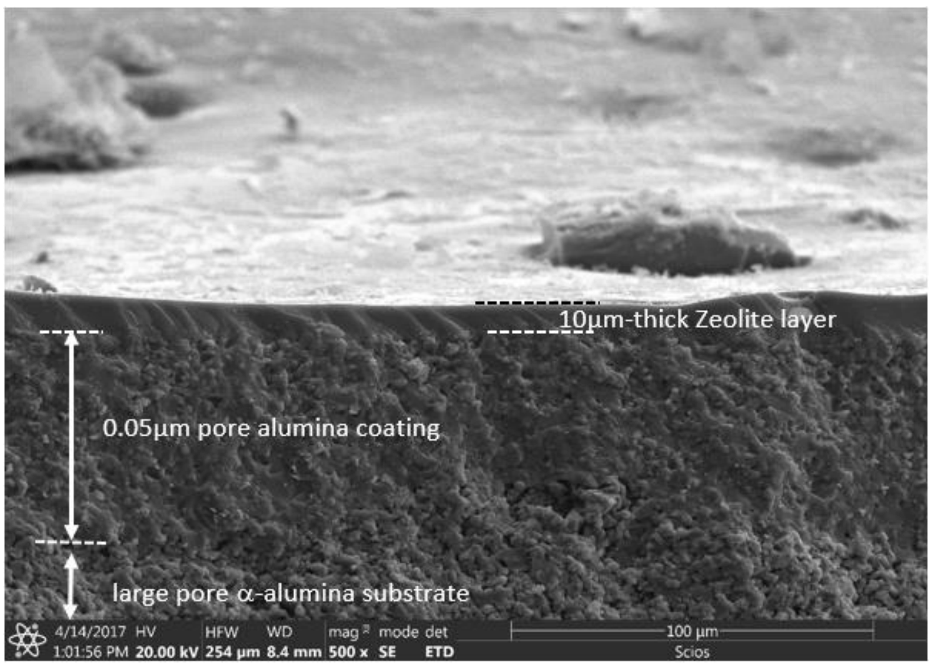
Conditions:

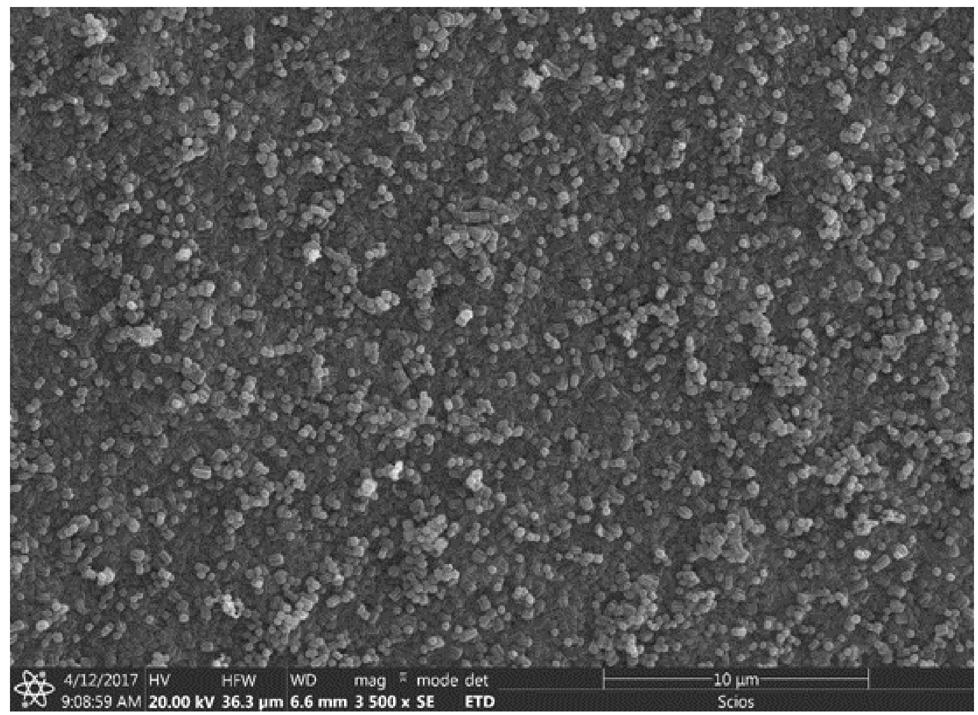
- T=500°C,
- H_2O/CO=3-3.5

Experimental Study on WGS in Lab-Scale Tubule Zeolite Membrane Reactor (Task 2.0) (Cont'd)

Morphology of Zeolite Membranes

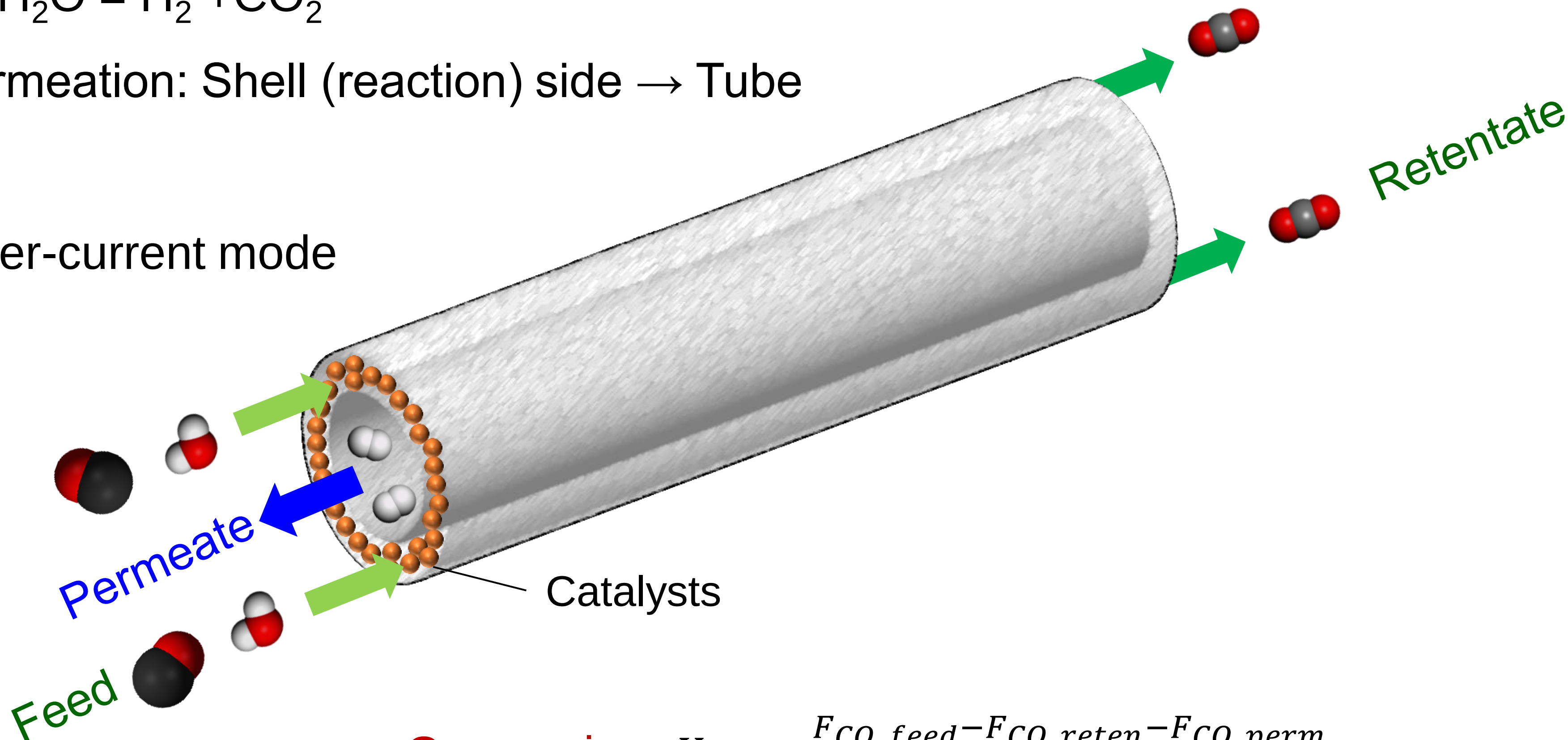
A 10-cm long tubular MFI zeolite membrane was tested for more than six months under WGS reaction conditions at 500^{o}C and reaction side pressure up to 26.5 bar. It was tested for over one week of WGS operation with feed CO containing 1,000 ppm of H_2S.





Modeling and Analysis for WGS in Zeolite Tubule Membrane Reactor (Task 3.0)

- $CO + H_2O = H_2 + CO_2$
- H_2 permeation: Shell (reaction) side → Tube side
- Counter-current mode



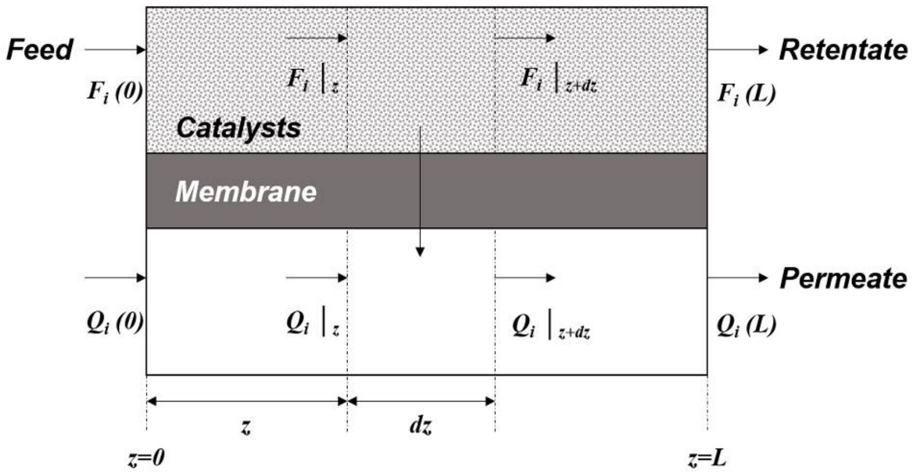
Conversion: $X_{CO} = \frac{F_{CO,feed} - F_{CO,reten} - F_{CO,perm}}{F_{CO,feed}}$

Purity: $G_{H_2} = \frac{F_{H_2,perm}}{F_{total,perm}}$, $G_{CO_2} = \frac{F_{CO_2,reten}}{F_{total,reten}}$

Recovery: $R_{H_2} = \frac{F_{H_2,perm}}{F_{H_2,reten} + F_{H_2,perm}}$

Capture: $R_{CO_2} = \frac{F_{CO_2,reten}}{F_{CO_2,reten} + F_{CO_2,perm}}$

Modeling and Analysis for WGS in Zeolite Tubule Membrane Reactor (Task 3.0) (Cont'd)



Assumptions/Considerations

(1) steady-state operation;

(2) plug flow;

(3) non-isothermal;

(4) negligible pressure drop along axial direction.

Basic equations

Feed stream:

$$\frac{dF_i}{dz} = v_i R w_{cat} - sP_i(x_i p_h - y_i p_l)$$

Permeate stream:

$$\frac{dQ_i}{dz} = sP_i(x_i p_h - y_i p_l)$$

Reaction rate (Co-Mo catalyst)

$$R = 0.008 \pm 0.0004\exp\left(\frac{-60.3 \pm 1.3}{R'T}\right) P_{CO}^{0.75\pm0.12} P_{H_2O}^{0.31\pm0.08} P_{CO_2}^{-0.07\pm0.02} P_{H_2}^{-0.09\pm0.02}(1-\beta)$$

$$\beta = 1/K \cdot P_{CO_2} P_{H_2} / P_{CO} P_{H_2O}$$

Ref.: Int J Hydrogen Energy 36 (2011) 6638–6645.

Parameters for simulation

Membrane characteristics:

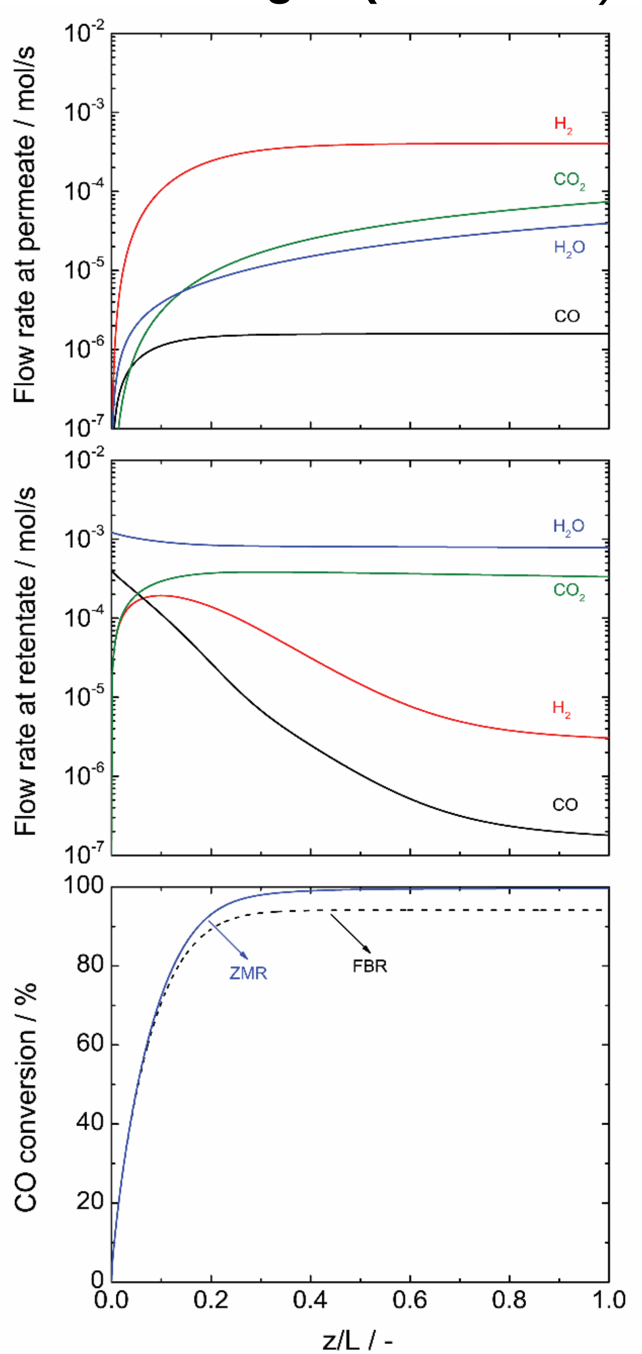
Membrane length = 0.250 m,
Membrane area = 0.0045 m^2,
P_{H2} = 150-600 GPU;
$\alpha(H_2/CO_2)$ = 15-45,
$\alpha(H_2/H_2O)$ = 200.

Operating conditions:

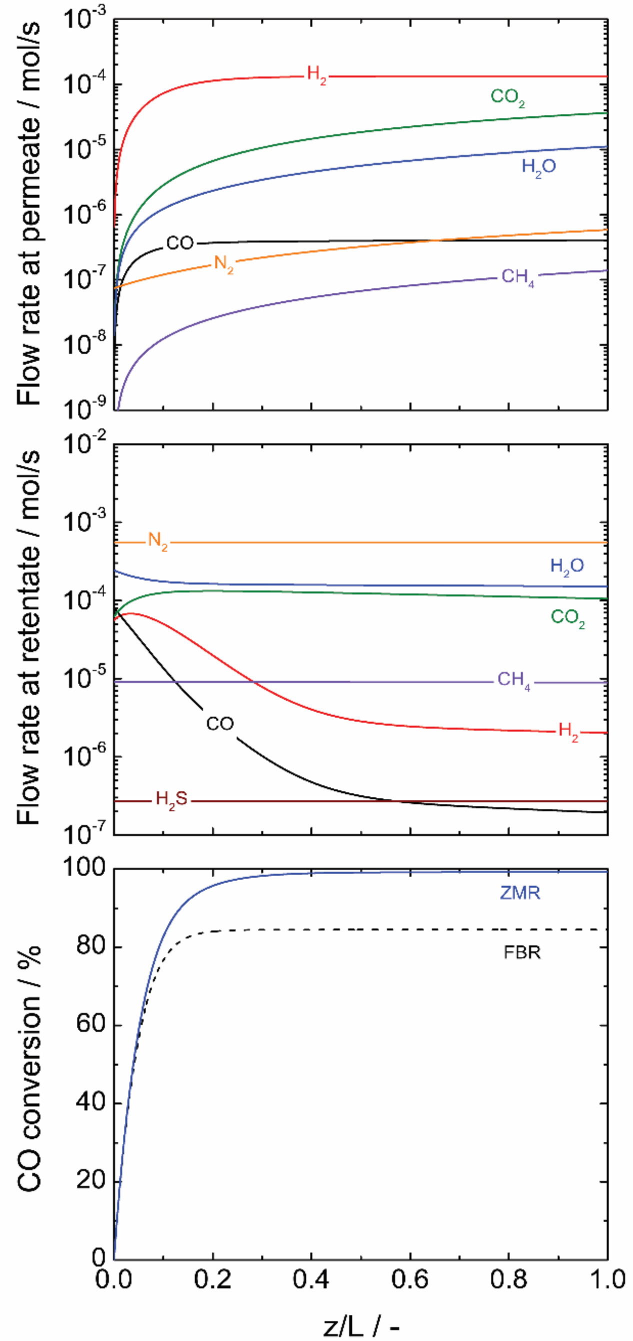
Steam/CO molar ratio: 1.5-3.0,
Temperature: 350-500 ^oC,
$P_{reten.}$ = 15-30 bar, $P_{perm.}$ = 10 kPa,
F_{feed} = 1.35 L/min.

Modeling and Analysis for WGS in Zeolite Tubule Membrane Reactor (Task 3.0) (Cont'd)

Simulated gas (Lab-scale)



Syngas at NCCC (Bench-scale)



H_2 purity in Permeate

- Lab-scale: > 84%
- Bench-scale: > 78%

CO_2 purity in Retentate

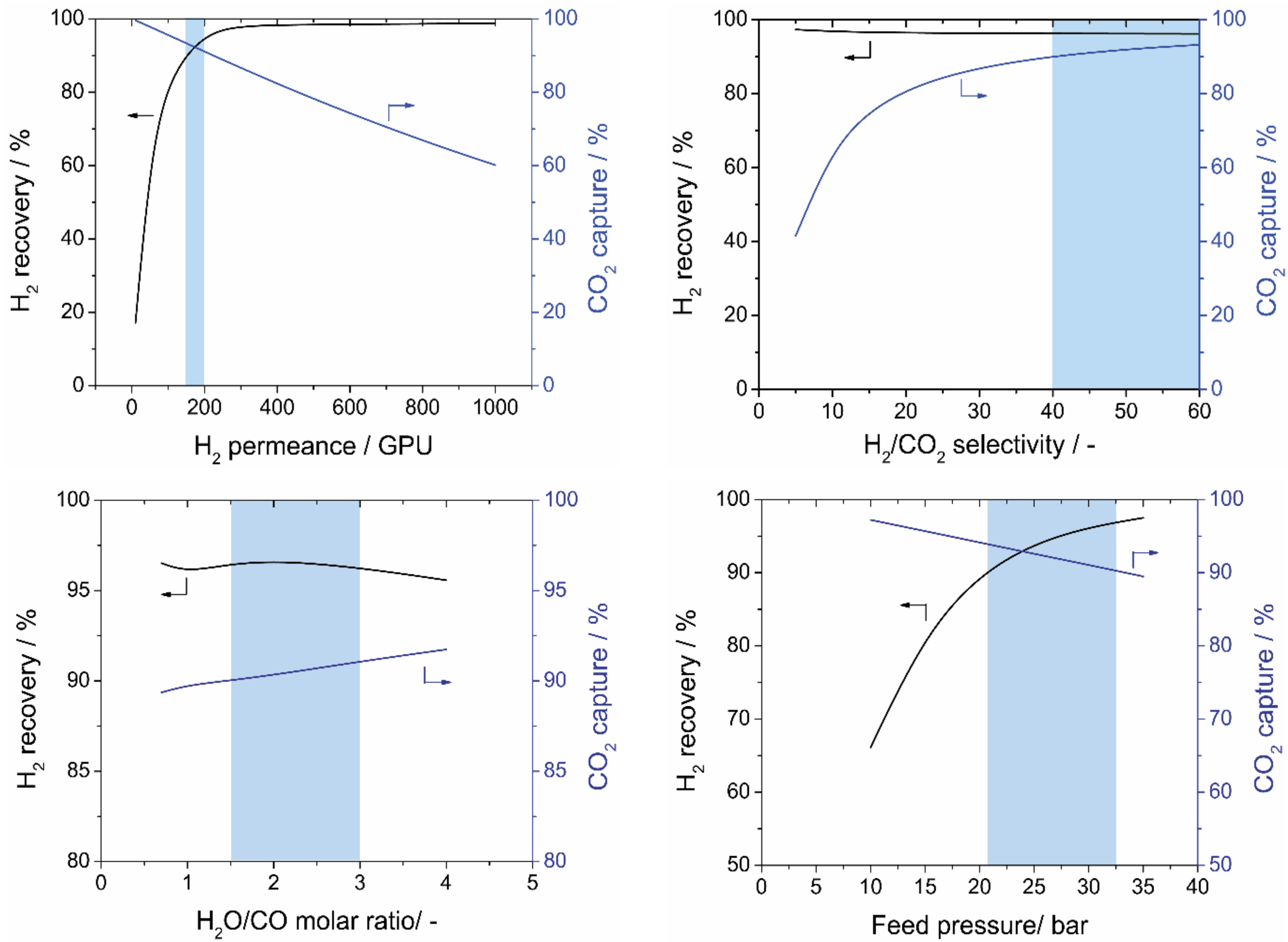
- Lab-scale: > 99%
- Bench-scale: < 16%

CO conversion

- FBR: $X_{CO,b} < X_{CO,l} < 92\%$
- ZMR: $X_{CO,b} = X_{CO,l} > 99\%$

Modeling and Analysis for WGS in Zeolite Tubule Membrane Reactor (Task 3.0) (Cont'd)

H_2 recovery > 92% & CO_2 capture > 90%



Optimizing Tubule Support Fabrication (Task 4.0)

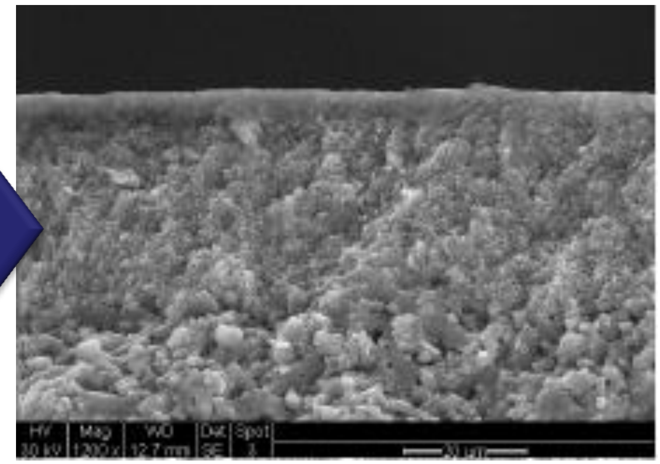
Ceramic Tube Extrusion

Intermediate Layer Deposition
+
Non-porous Tip and End Seals

End Seal (Open end)

Tip Seal (Closed end)

Zeolite Layer Deposition
+
(Silica CCD Modification)



Package into Multiple Tube Bundle
+
(Silica CCD Modification)

MPT 57-tube Bundle (Carbon Molecular Sieve Membrane)

Optimizing Tubule Support Fabrication (Task4.0) (Cont'd)

Challenge Conditions: *T = 180°C; up to 48 hours; various NaOH and Zeolite Synthesis solution*

Exposure to high pH and high temperature for extended periods will impact tube strength

- *Approach #1: Nominal tube wall thicknesses of 1.1, 1.45, and 1.75mm tested*
- *Approach #2: Higher alumina content in tube (99%)*

Conclusion ***Thicker wall tube may be appropriate but not required.***

Part ID	Wall Thickness [mm]	Tube Strength, 3-point Bend Test [psi]				
		As-Produced	1.4% NaOH 6 hours 180°C	1.4% NaOH 48 hours 180°C	2.7% NaOH 48 hours 180°C	Zeolite Synthesis Solution 18 hours 180°C
Standard Tube	1.1	39.8	33.7	33.2	25.1	32.3
Approach #1, Increase strength with thicker wall tube						
Thick Wall #1	1.5	59.2	48.0	48.3	32.4	47.1
Thick Wall #2	1.8	73.2	57.0	55.3	41.8	54.7
Approach #2, Increase chemical resistance with high purity alumina						
99% #1	1.1	30.5		29.4		
99% #2	1.1	35.2		34.2		

1. ***Target strength** required for finished zeolite membrane tube is based upon MPT commercial experience with the 1.1mm wall standard part.*

2. ***Post challenge testing strength** of the 1.5mm wall thickness tube is superior to the "unchallenged" MPT standard membrane.*

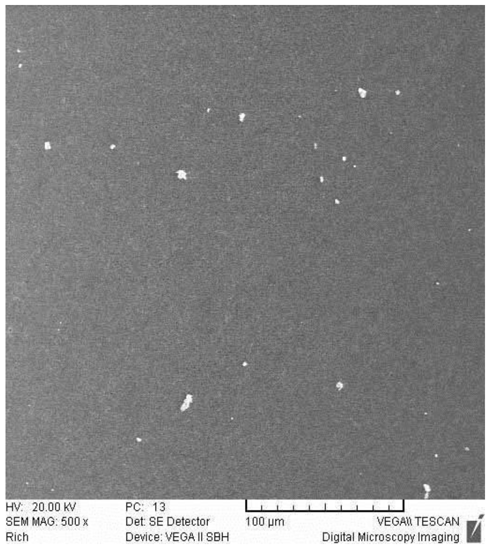
Optimizing Tubule Support Fabrication (Task 4.0) (Cont'd)

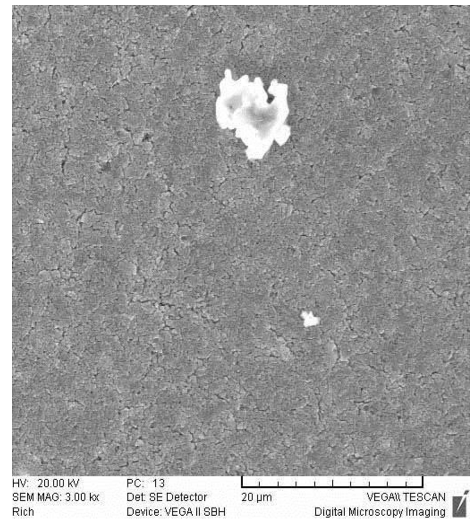
Demonstrate Substrate Intermediate Layer Integrity/ Material Stability in Zeolite Synthesis Solution

Challenge Conditions: *T = 180°C; 48 hours; 2.7% NaOH*

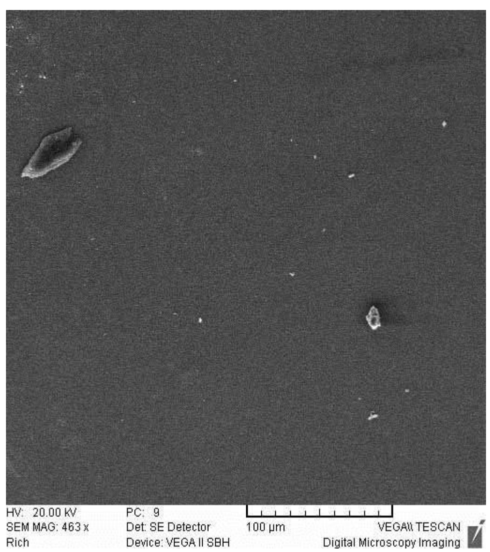
Conclusion *No impact on intermediate layer quality*

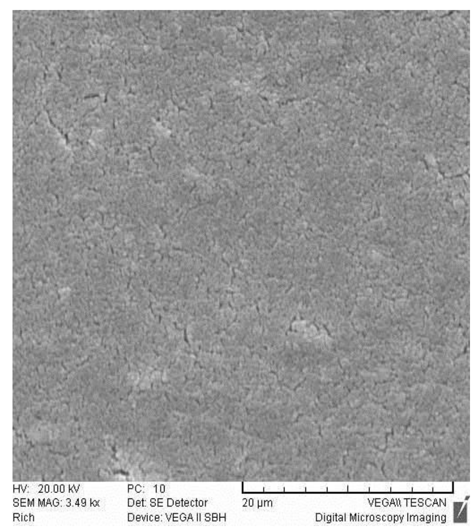
Intermediate Layer
Pre-challenge Testing
0.05µm Pore Size
500x and 3,000x





Intermediate Layer
Post NaOH Challenge
0.05µm Pore Size
500x and 3,000x



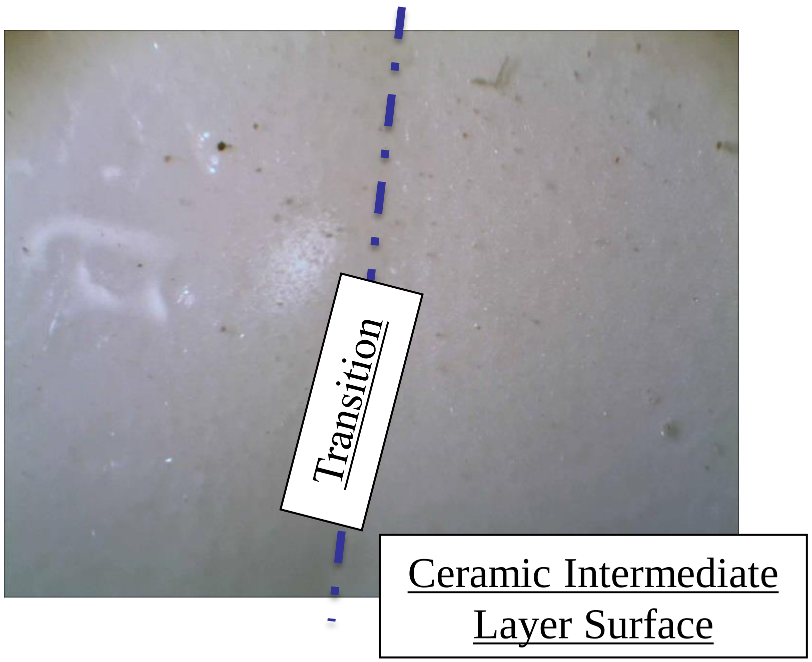


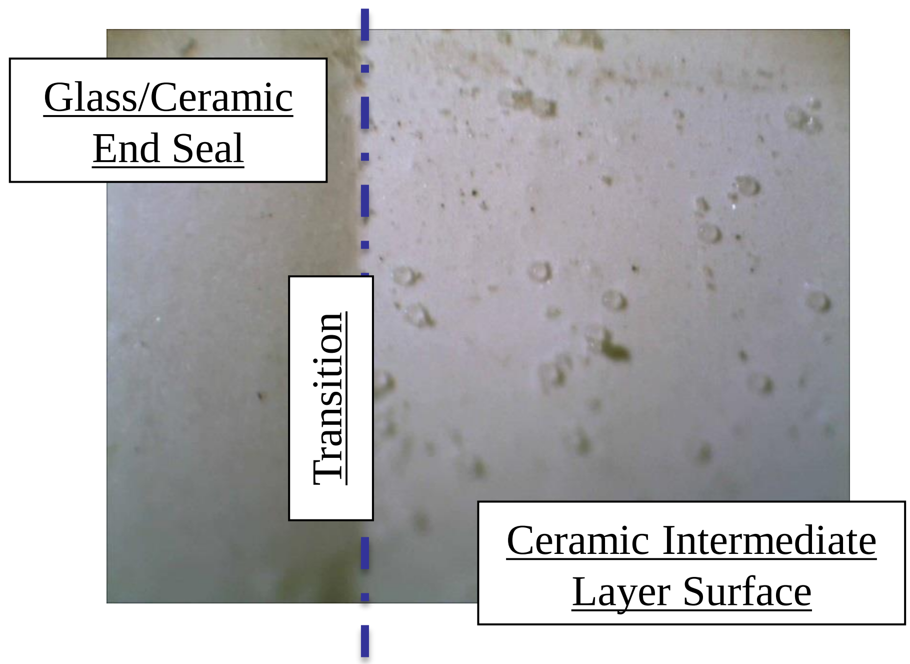
Optimizing Tubule Support Fabrication (Task 4.0) (Cont'd)

Demonstrate Ceramic/Glass Sealant Material Stability in Zeolite Synthesis Solution

<u>Challenge Conditions:</u> T = 180^{o}C; 48 hours; 2.7% NaOH

Conclusion





Optimizing Tubule Support Fabrication (Task 4.0) (Cont'd)

Demonstrate High Temperature Hydrothermal Stability of Membrane Bundle Components and Seals

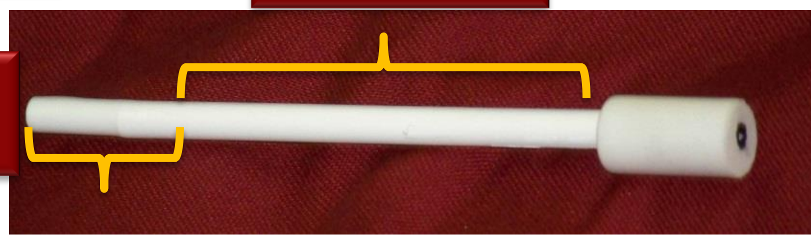
Single Tube Bundle

Operating Conditions: T = 450°C; P = 300 psig; Steam = 80% (in N_2)

Three Primary Scale-up Seal Components

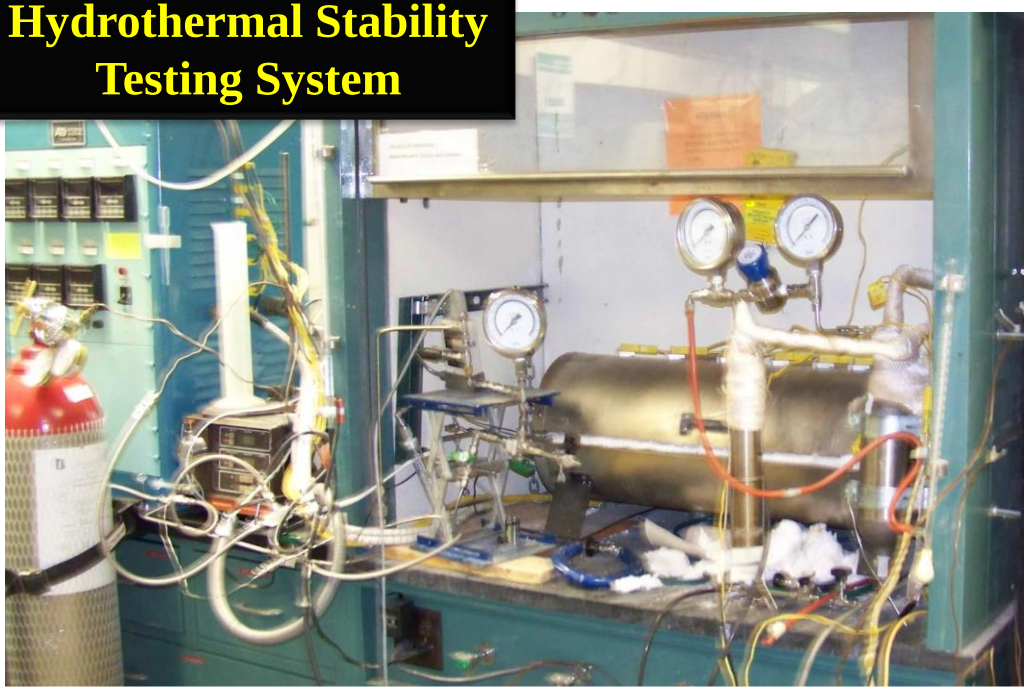
Impermeable End Seal

Ceramic Tip



Ceramic Tube Sheet and Ceramic/Glass Potting

Hydrothermal Stability Testing System



Results/Conclusions

1. *No leak development over 185 days of hydrothermal stability challenge testing.*
2. *All seal component appear to be stable in the testing conditions.*

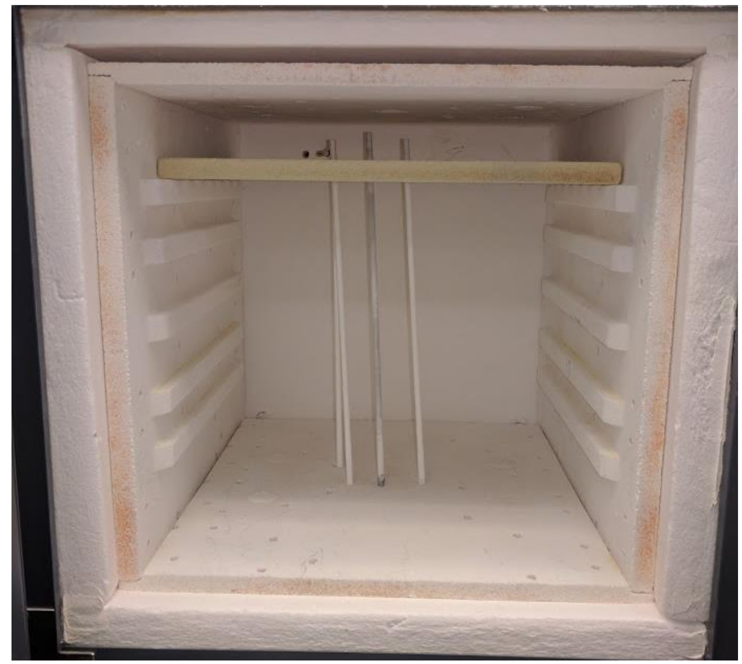
Optimizing Zeolite Membrane Synthesis Methods (Task 5.0)

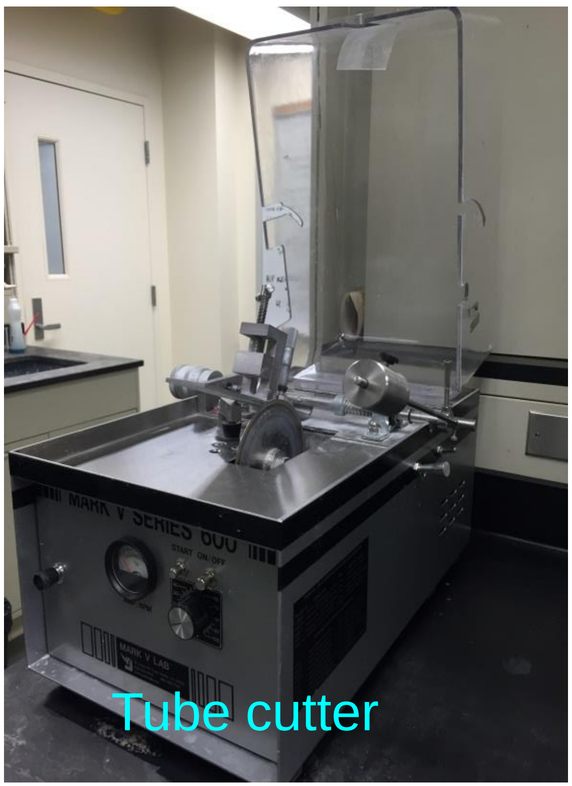
<u>Facility Establishment (design and construction):</u>

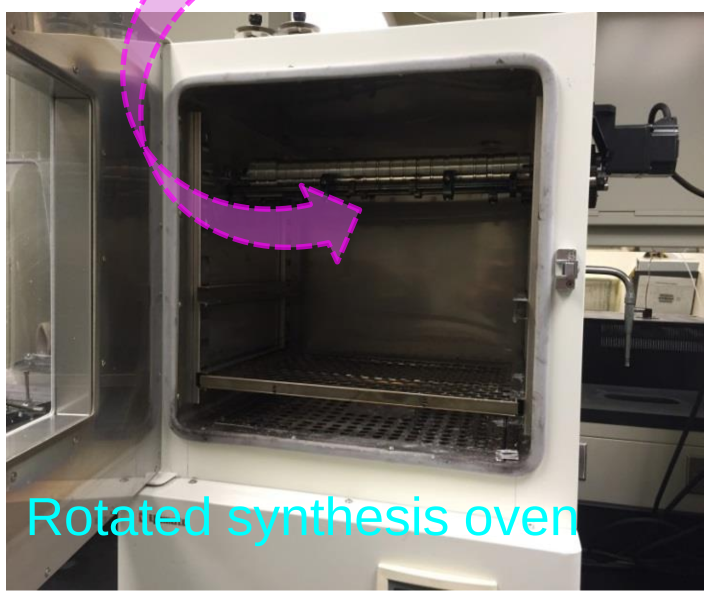
- Long tube hydrothermal synthesis and membrane activation systems

Synthesis vessels for 10-am and 35-cm long tubes

Large furnace for 35-cm long tube activation



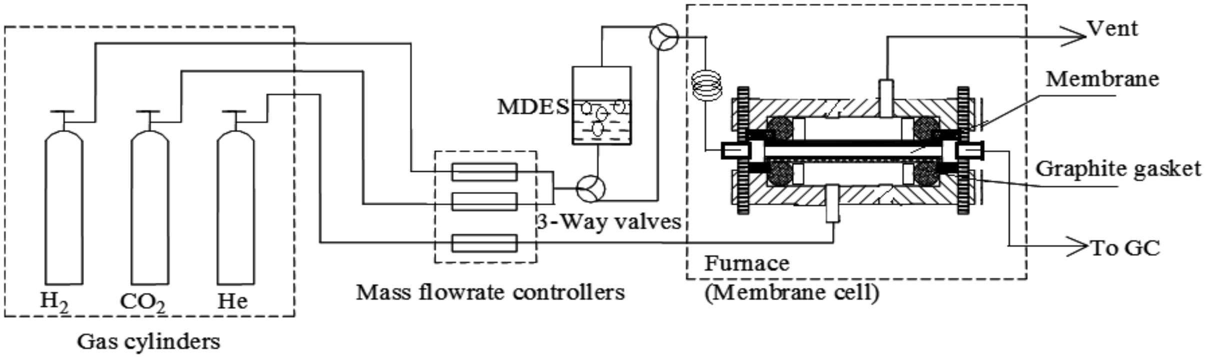


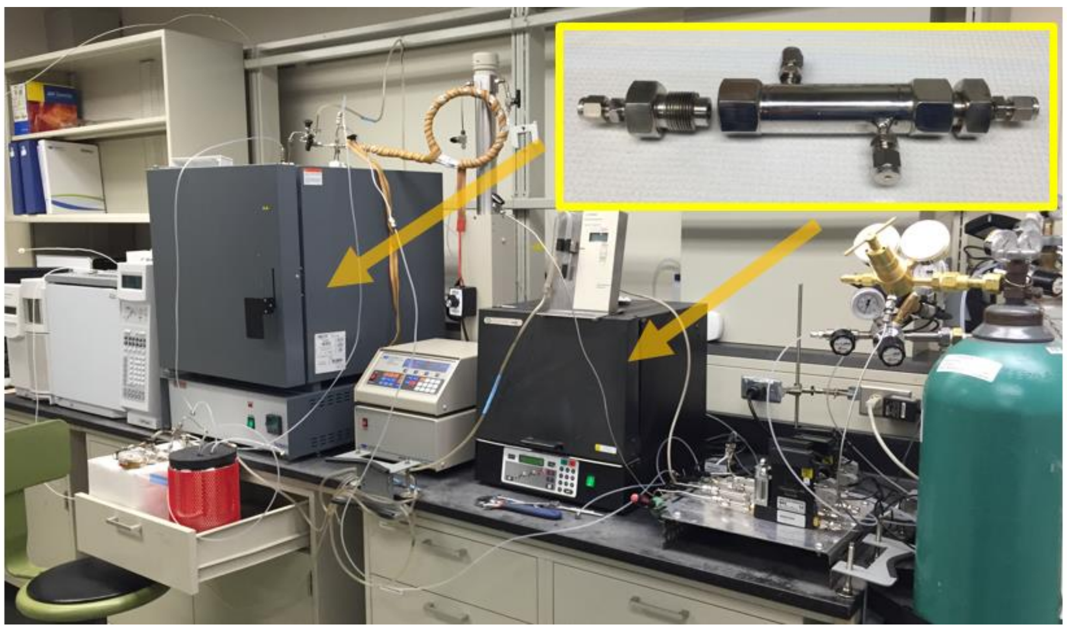


Optimizing Zeolite Membrane Synthesis Methods (Task 5.0) (Cont'd)

Facility Establishment (design and construction):

- Membrane modification, stability test and WGS reaction system





High temperature high pressure
Membrane modification, test, and WGS reaction

Long term stability
testing system

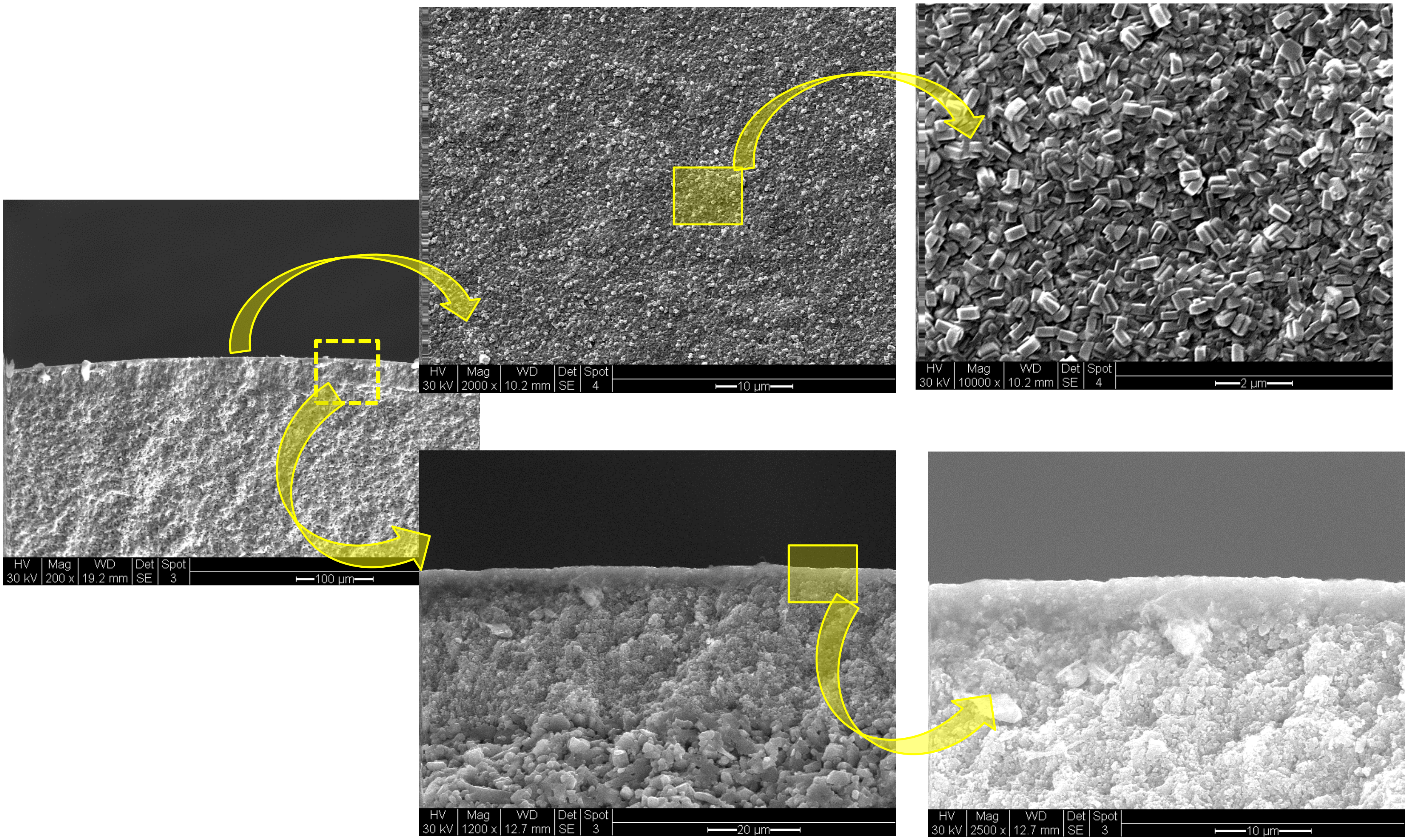
Optimizing Zeolite Membrane Synthesis Methods (Task 5.0) (Cont'd)

— Best results achieved via in-situ synthesis with solutions of high pH (NaOH) for hydrothermal synthesis and two-step CCD modification at 450 – 500C.

Method	Hydrothermal precursor	Seed layer	Conditions (hydrothermal & CCD modification)	Quality before CCD	Quality post CCD
In situ	SiO_2+H_2O+ NaOH+TPAOH	No	Hydrothermal: 180C/8h/rotation CCD: 450 – 500C; two-step	Excellent	Excellent $\alpha_{H2/CO2}$ ~ 20 - 50
In situ	SiO_2+H_2O+ $AlCl_3$+NaOH +TPAOH	No	Hydrothermal: 180C/6h/rotation CCD: 450; two-step	Good	Good $\alpha_{H2/CO2}$ ~ 10 - 20
Secondary growth	TEOS+H_2O+ $AlCl_3$+NaOH +TPAOH	Yes; Silica-lite	Hydrothermal: 165C/6h/rotation CCD: 450C; two-step	Excellent	Good $\alpha_{H2/CO2}$ ~ 12
Secondary growth	TEOS+H_2O+ $AlCl_3$+NaOH +TPAOH	Yes; ZSM-5	Hydrothermal: 165C/6h/rotation CCD: 450C; two-step	Average	Poor $\alpha_{H2/CO2}$ < 10

Optimizing Zeolite Membrane Synthesis Methods (Task 5.0) (Cont'd)

ZSM-5 Membranes on MPT Tubes

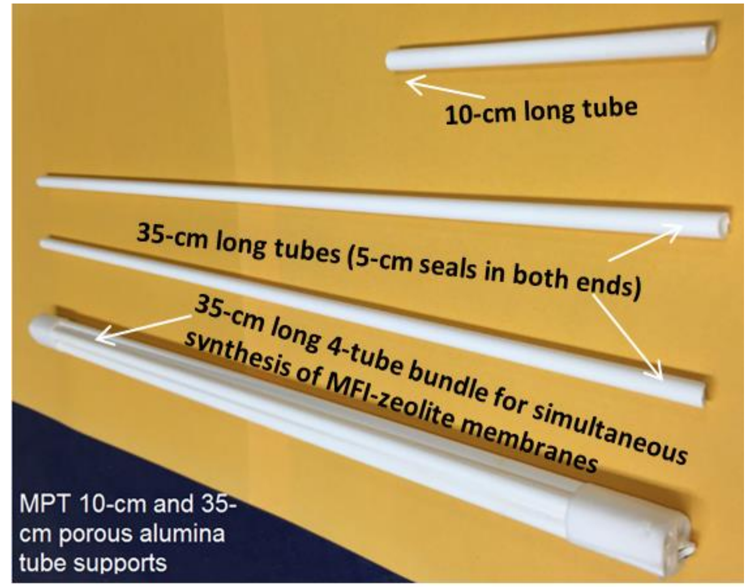


Scaling up Synthesis of High Quality Zeolite Membranes (Task 6.0)

Previous synthesis of 2.5-cm-diameter disc and 2-cm long ϕ1.0-cm tube (Pall Corp) membranes

Different size and geometry and surface chemistry of MPT tubes needs changes in: (1) zeolite precursor chemistry, (2) hydrothermal synthesis conditions, (3) calcination conditions, and (4) CCD modification conditions

Synthesis of 10-cm long ϕ1.0-cm tube (Pall Corp) membranes

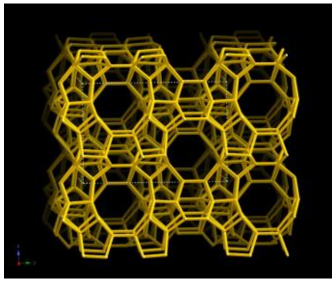


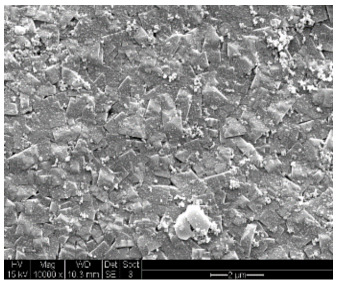
Long tube and multi-tube synthesis (dead-ended and open-ended): (1) zeolite precursor chemistry, (2) hydrothermal synthesis conditions, (3) calcination conditions, and (4) CCD modification conditions

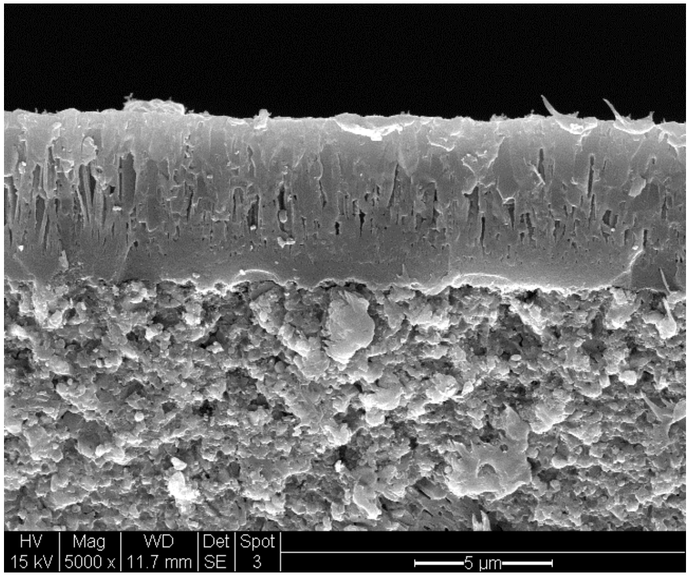
Preparation of 35-cm long tube membranes on MPT ϕ=0.57-cm tubes and scale-up to making multi-tubes in single batch

Scaling up Synthesis of High Quality Zeolite Membranes (Task 6.0) (Cont'd)

Mechanisms of CCD of Modification of Zeolite Membrane using MDES







(1) Chemisorption :

$$CH_3(C_2H_5O)_2SiH + HO\text{-}Si{\equiv} \longrightarrow C_2H_5OH + CH_3(C_2H_5O)HSi\text{-}O\text{-}Si{\equiv}$$

$$CH_3(C_2H_5O)_2SiH + HO\text{-}Si{\equiv} \longrightarrow H_2 + CH_3(C_2H_5O)_2Si\text{-}O\text{-}Si{\equiv}$$

$$CH_3(C_2H_5O)_2SiH + HO\text{-}Si{\equiv} \longrightarrow CH_4 + (C_2H_5O)_2HSi\text{-}O\text{-}Si{\equiv}$$

(2) Water induced decomposition [23]:

$$CH_3(C_2H_5O)HSi\text{-}O\text{-}Si{\equiv} + H_2O \longrightarrow H_2 + CH_3(C_2H_5O)(OH)Si\text{-}O\text{-}Si{\equiv}$$

$$CH_3(C_2H_5O)(OH)Si\text{-}O\text{-}Si{\equiv} + H_2O \longrightarrow CH_4 + (C_2H_5O)(OH)_2Si\text{-}O\text{-}Si{\equiv}$$

$$CH_3(C_2H_5O)_2Si\text{-}O\text{-}Si{\equiv} + H_2O \longrightarrow CH_4 + (C_2H_5O)_2(OH)Si\text{-}O\text{-}Si{\equiv}$$

$$(C_2H_5O)_2HSi\text{-}O\text{-}Si{\equiv} + H_2O \longrightarrow H_2 + (C_2H_5O)_2(OH)Si\text{-}O\text{-}Si{\equiv}$$

$$(C_2H_5O)_2(OH)Si\text{-}O\text{-}Si{\equiv} + H_2O \longrightarrow C_2H_5OH + (C_2H_5O)(OH)_2Si\text{-}O\text{-}Si{\equiv}$$

$$(C_2H_5O)(OH)_2Si\text{-}O\text{-}Si{\equiv} + H_2O \longrightarrow C_2H_5OH + (OH)_3Si\text{-}O\text{-}Si{\equiv}$$

(2) Thermal decompsoition/termination [23]:

$$(C_2H_5O)(OH)_2Si\text{-}O\text{-}Si{\equiv} \longrightarrow H_2O + (C_2H_5O)OSi\text{-}O\text{-}Si{\equiv}$$

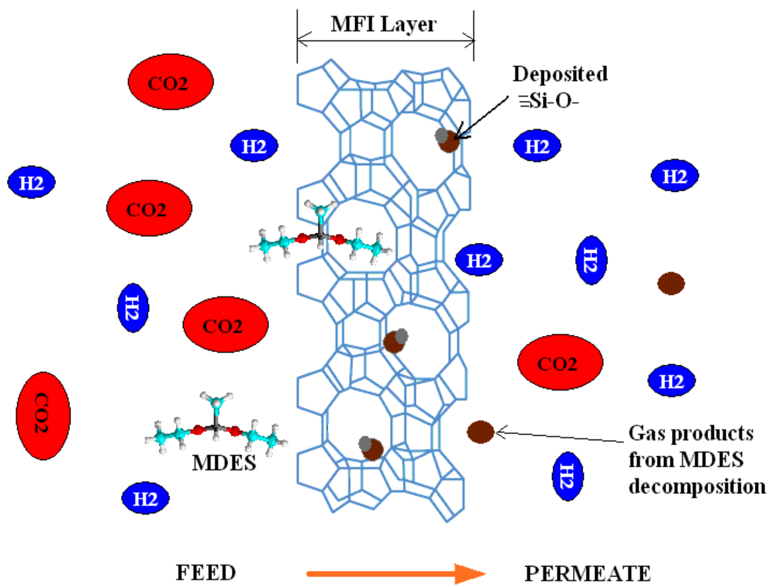
$$\longrightarrow C_2H_4 + (OH)_3Si\text{-}O\text{-}Si{\equiv}$$

$$\longrightarrow H_2O + (OH)OSi\text{-}O\text{-}Si{\equiv}$$

(3) Side reactions:

$$H_2 + CO_2 \leftrightarrow H_2O + CO \quad (HT)$$

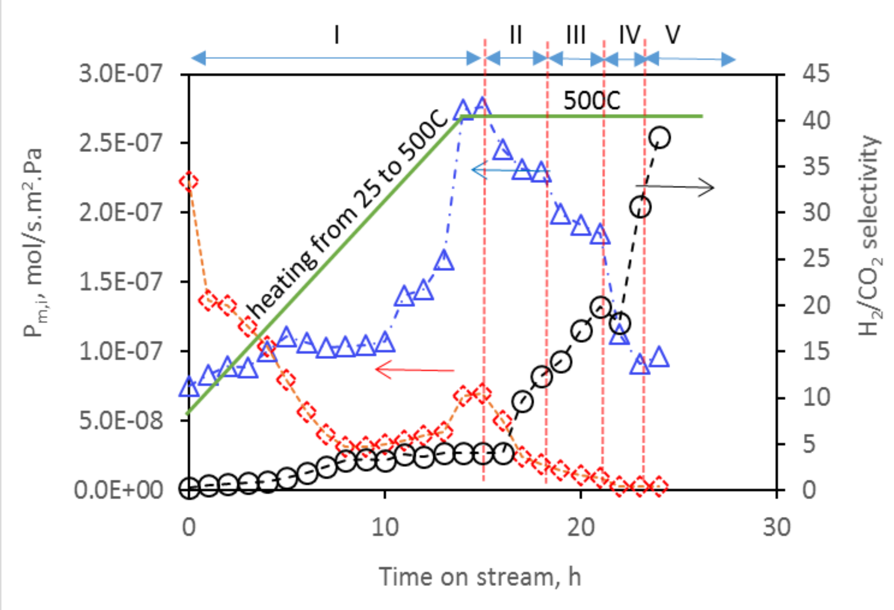
$$C_2H_5OH \longrightarrow C_2H_4 + H_2O \qquad (\text{cat. at} >200^{\circ}C)$$



Ref: O'Connor, Moller, Manstein, CatTech 2001, 5, 172; Masuda, Fukumoto, Kitamura, Micropor. Mesopor. Mater. 2001, 48, 239; Tang, Nenoff, Dong, *Langmuir* 2009, *25*,4848.

Scaling up Synthesis of High Quality Zeolite Membranes (Task 6.0) (Cont'd)

Modified Membrane Properties



Evolution of the H_2 and CO_2 ($P_{m,i}$) permeance and H_2/CO_2 separation factor ($\alpha_{H2/CO2}$) during the two-step process of CCD modification of the tubular MFI zeolite membrane: (I) ramping from 25 to 500°C and dwelling for 2 h at 500°C; (II) MDES vapor introduced; (III) MDES feed stopped; (IV) MDES vapor introduced for the second time; and (V) MDES vapor feed stopped –

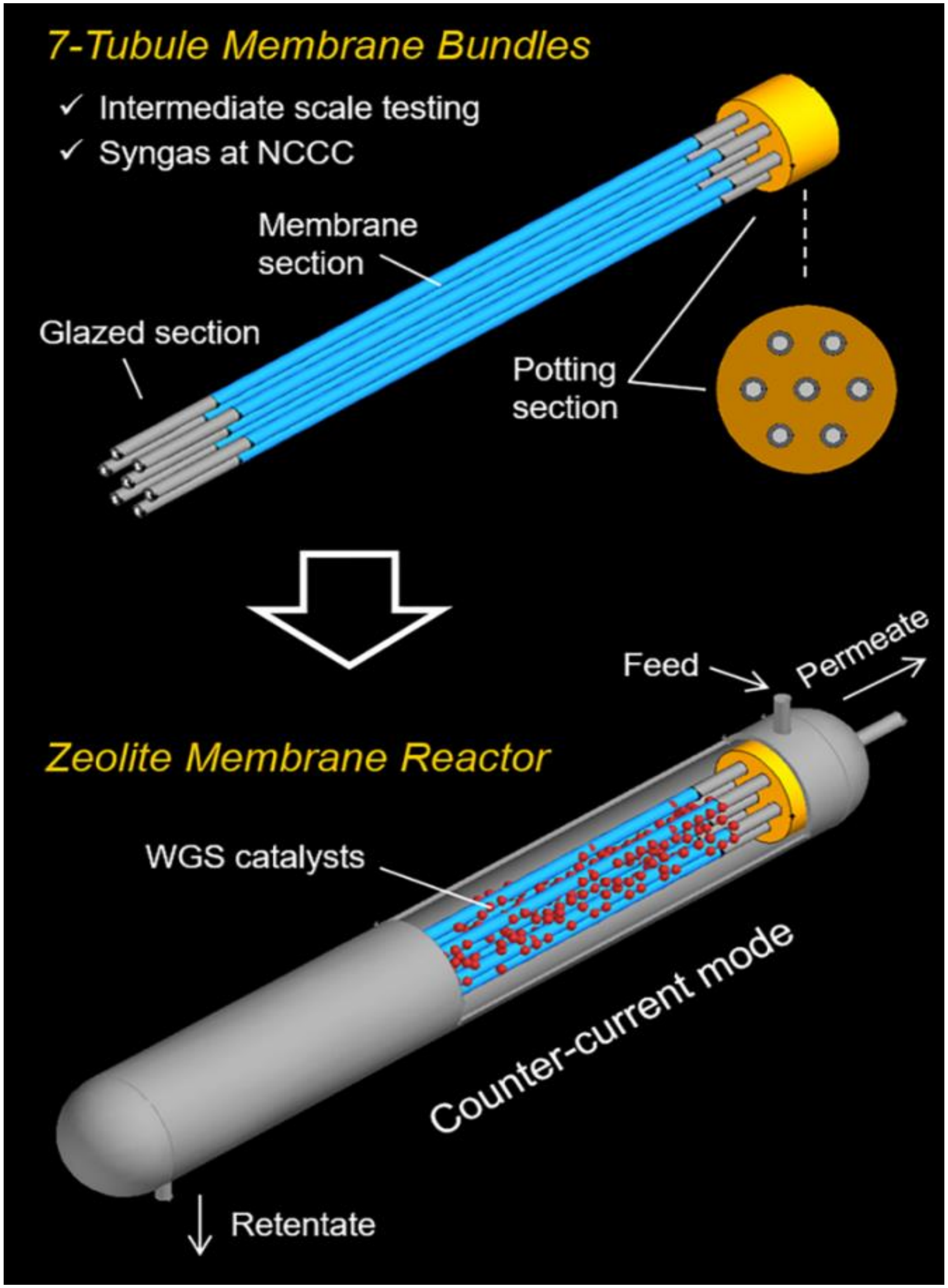
CCD modification completed.

Performances demonstrated on the modified MFI zeolite membranes of different scale up stages – for separating 50v/50v H_2/CO_2 mixture at 450°C and 1 atm (1GPU=3.35×10^{-10} mol/m^2·s·Pa)

Support	Dimensions	Support Maker	A_m (cm^2)	$\alpha_{H2/CO2}$	$P_{m,H2}$ (GPU)	Target	
						$\alpha_{H2/CO2}$	$P_{m,H2}$ (GPU)
Disc	D = 2.5-cm	UC lab	2.5	62	~390	--	--
Tube	L=8cm; L_m =1.5 cm; OD=1cm; ID=0.7 cm	Pall Co.	4.7	>100	~806	--	--
Tube	L=8cm; L_m =6 cm; OD=1cm; ID=0.7 cm	MPT	11.0	45±5	360±50	45	600
Tube	L=35cm; L_m =25 cm; OD=1cm; ID=0.7 cm	MPT	44.8	41±5	725±50	45	600

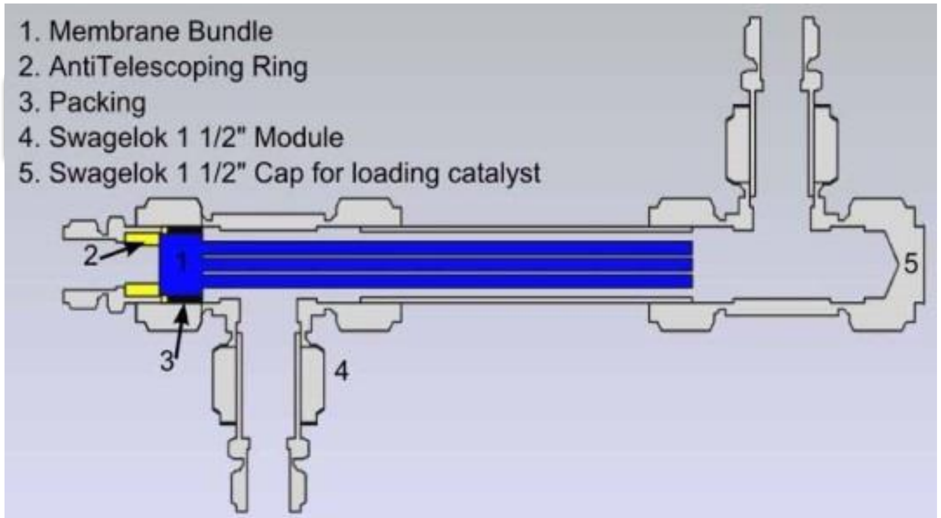
Design and Fabrication of Zeolite Membrane Bundles and Modules (Task 7.0)

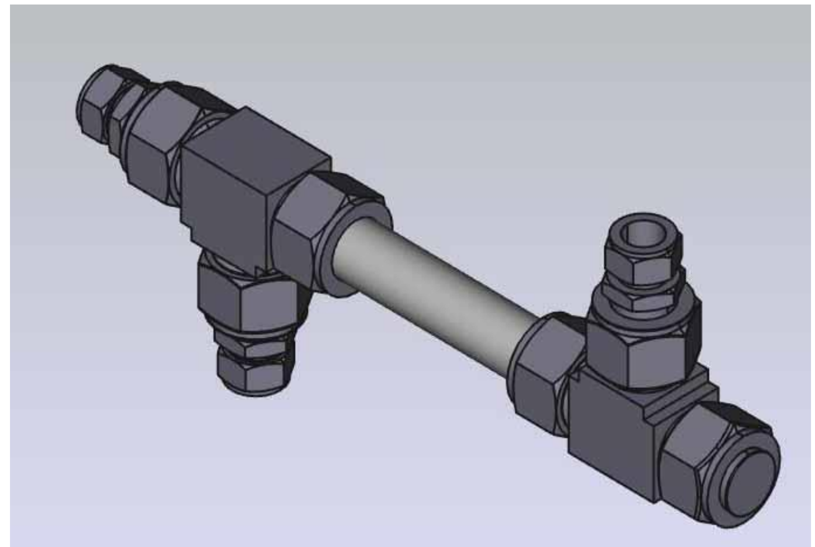
Single, 3- and 7-tube alumina membrane "bundles" for use in the high temperature hydrothermal pressure testing.

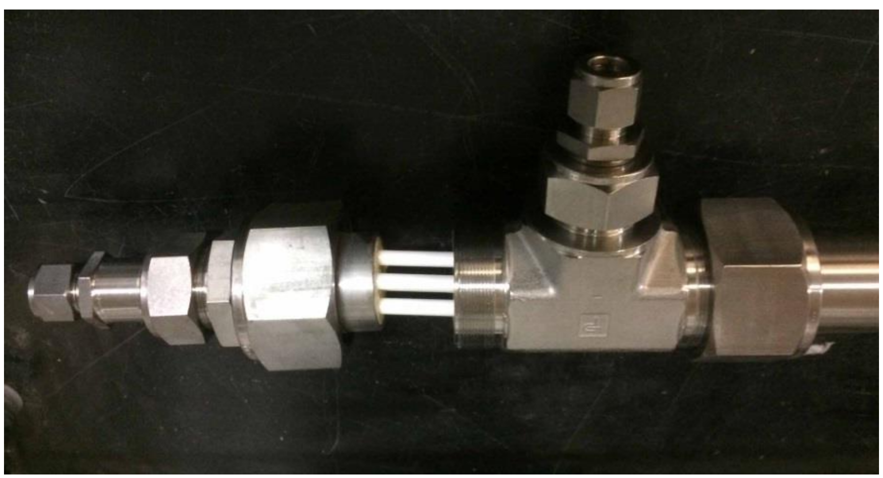


Design and Fabrication of Zeolite Membrane Bundles and Modules (Task 7.0) (Cont'd)

7-Tube Bundle Module and Reactor



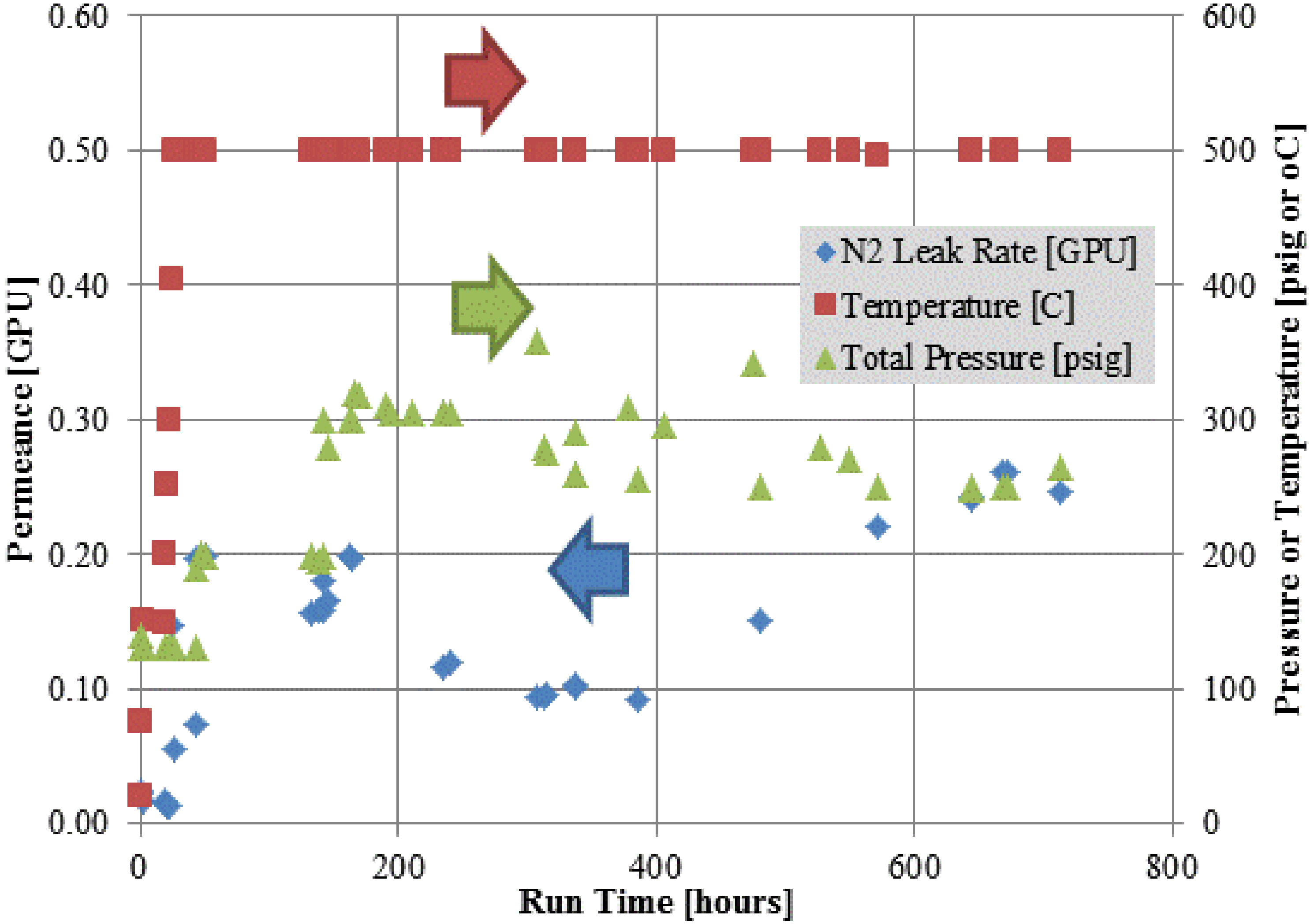




Design and Fabrication of Zeolite Membrane Bundles and Modules (Task 7.0) (Cont'd)

Demonstrate High Temperature Hydrothermal Stability of Membrane Bundle Components and Seals ***Scale-up to 7-Tube Bundle***

Operating Conditions: ***T = 500°C; P = 300 psig; Steam = 80% (in N_2)***



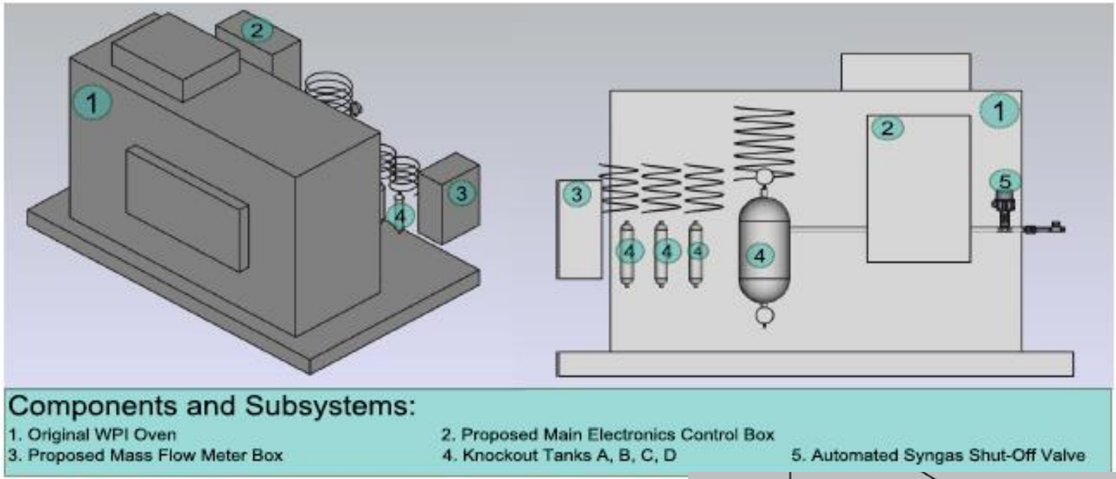
Testing Zeolite Tube Bundles under Gasifier Conditions Including Membrane Reactor Configuration (Task 8.0)

Modify NCCC Test Rig for Gasifier Off-gas Challenge Testing of Zeolite Membrane and Bundle Components and Seals ***Target Conditions:*** *450°C and 300psig; no pretreatment (NCCC max operating conditions available); Single tube, 7-tube, and 21-tube bundles*

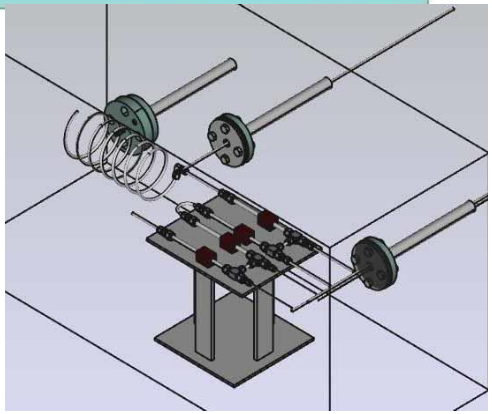
WPI/MTR skid: *Oven and system components approved for use by NCCC under proposed operating conditions.*

Interior dimensions
48w x 24h x 24 deep

MPT Modifications: *Target automated operation and remote monitoring for continuous long term testing of proposed membrane technology.*



MPT Modifications
Testing of several membrane bundles/modules simultaneously



Establishing Conceptual Process Design, Performance Model and Preliminary Techno-Economic Analysis of WGS Zeolite Membrane Reactor Technology (Task 9.0)

ZMR Integration Methodology

- ***Reference Case IGCC - Case 2 (GE Gasifier with Selexol AGR and GE F-class gas turbines) in the 2013 DOE/NETL Report 1397 on "Bituminous Coal and Natural Gas to Electricity, Rev 2a"***
- ***IGCC Design to NETL's QGESS Guidelines***
- ***Cost Estimation and Financial Modeling Methodology***
  - ***For process systems associated with the ZMR WGS and CO_2 capture technologies, Nexant will carry out preliminary process design to establish system performances and develop major equipment-factored capital costs. Costs for proprietary equipment will be provided by technology licensors.***
  - ***For process and support systems that are unrelated to the ZMR WGS and CO2 capture technology, performances and capital costs will be scaled from the NETL Reference Case 2 according to capacity factors established by process H&MB, and by overall utility and commodity material balances.***

Establishing Conceptual Process Design, Performance Model and Preliminary Techno-Economic Analysis of WGS Zeolite Membrane Reactor Technology (Task 9.0) (Cont'd)

TEA Design Basis

- *Illinois # 6 Design Coal Feed*
- *Mid West Site*
- *Fixed fuel HHV to two GE advanced F-class turbines, each generating 232 MW nominal (464 MW total) GT gross output*
- *800 psig GE Radiant-Cooled Slurry-Fed Gasification*
- *95% O_2 from Elevated Pressure Air Separation Unit*
- *Selexol Acid Gas Recovery*
- *CO_2 Purification, Drying & Compression to 2200 psig at Battery Limit for disposal by Saline Reservoir Injection*
- *All costs in 2011 dollars*

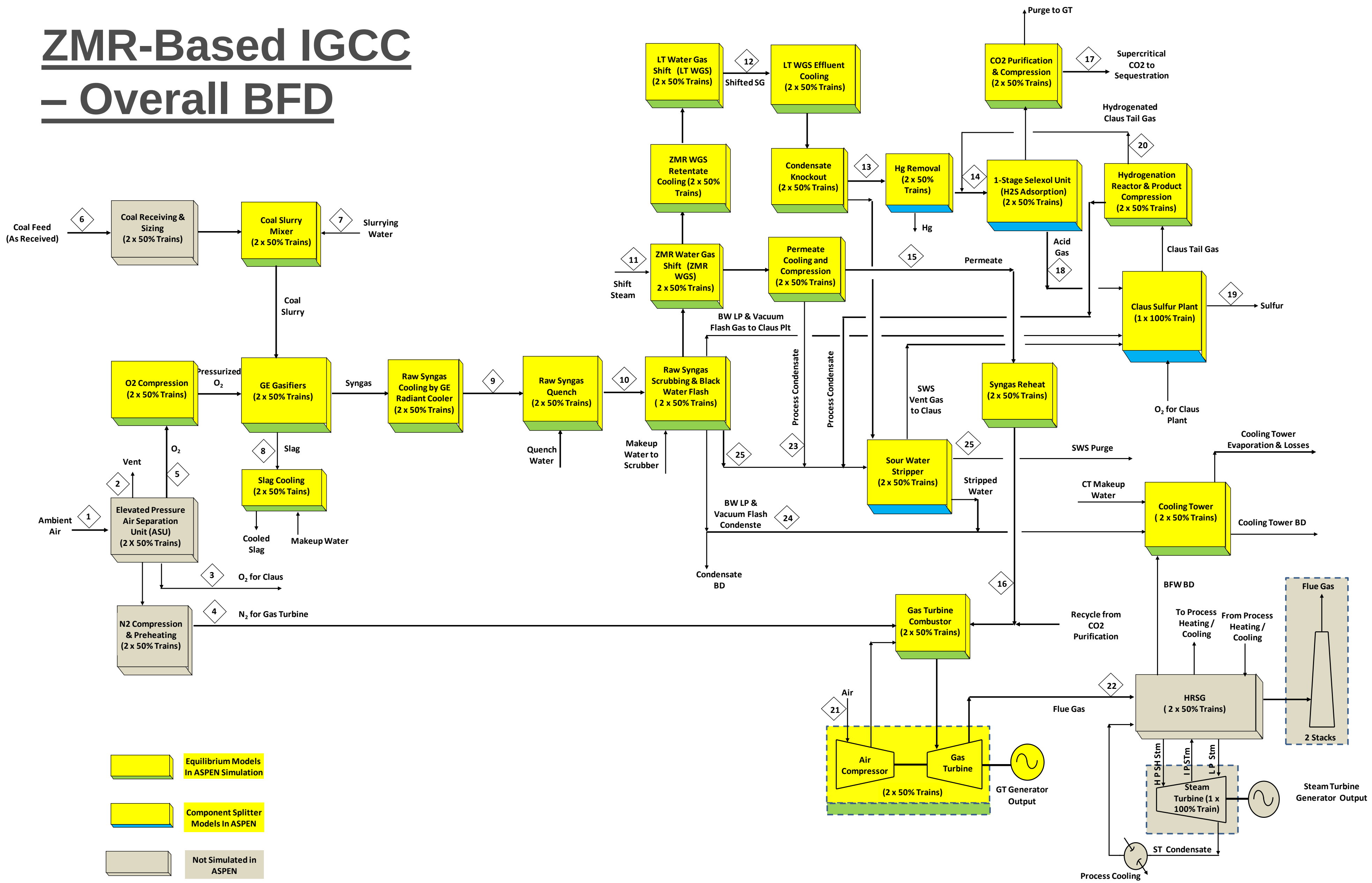
Establishing Conceptual Process Design, Performance Model and Preliminary Techno-Economic Analysis of WGS Zeolite Membrane Reactor Technology (Task 9.0) (Cont'd)

Design Assumptions

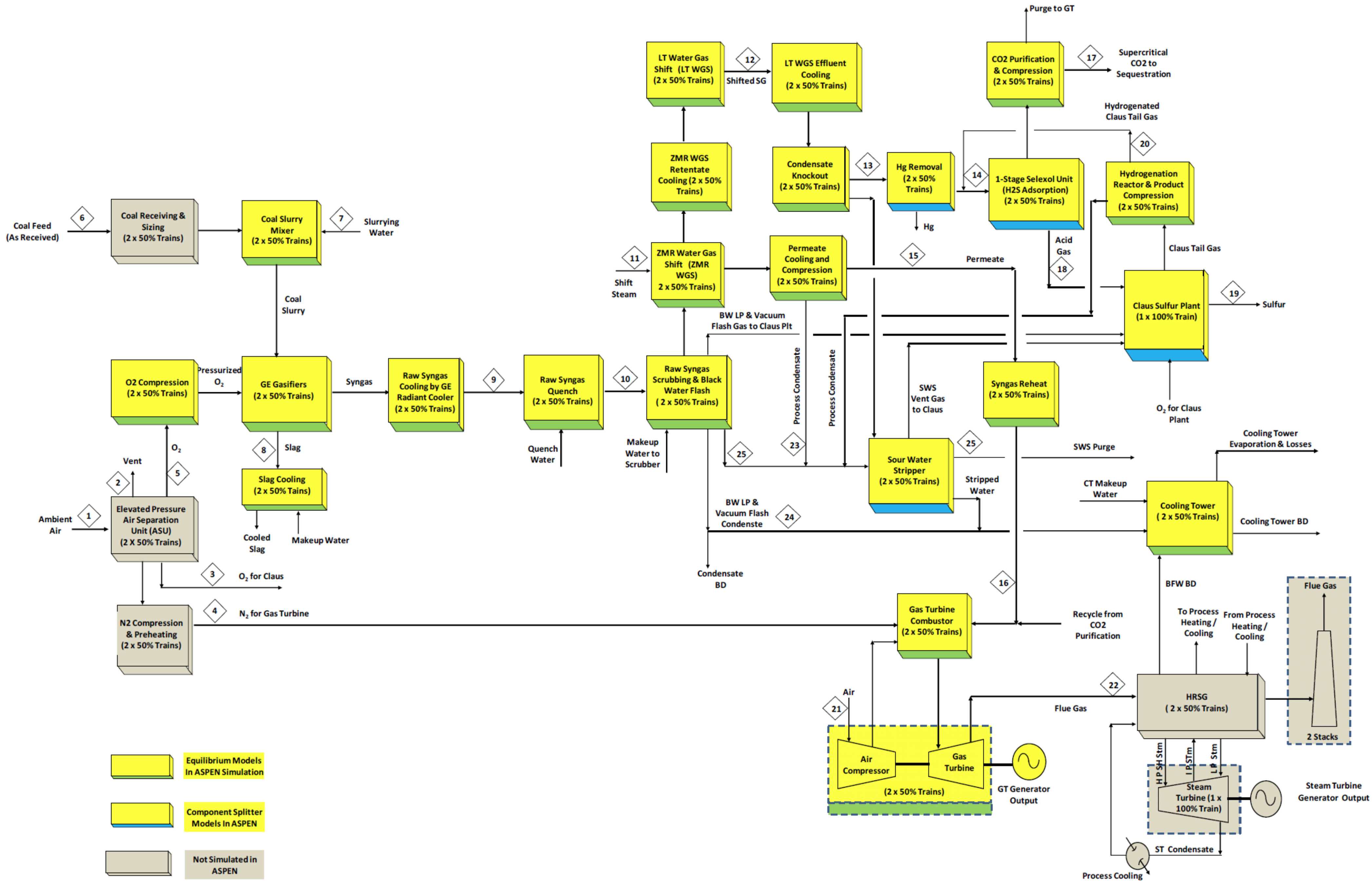
1) *FEED PRESSURE:*
   - *Published ZMR feed pressure = 34 barg (500 psig).*
   - *Assume ZMR can handle 800 psig operating pressure.*
2) *FEED H2S & COS:*
   - *ZMR has been tested for 400 ppmv H_2S & is expected to be good for 1,000 ppmv H_2S per FOA proposal.*
   - *Assume ZMR can operate at ~4,500 ppmv (8,000 ppmv dry) H_2S in feed.*
   - *Assume COS will be hydrolyzed to H_2S by the ZMR.*
3) *FEED HCL & NH3:*
   - *These are assumed to be removed by water scrubber upstream of ZMR.*

Establishing Conceptual Process Design, Performance Model and Preliminary Techno-Economic Analysis of WGS Zeolite Membrane Reactor Technology (Task 9.0) (Cont'd)

ZMR-Based IGCC – Overall BFD



ZMR-Based IGCC Overall BFD (Higher Resolution)



Establishing Conceptual Process Design, Performance Model and Preliminary Techno-Economic Analysis of WGS Zeolite Membrane Reactor Technology (Task 9.0) (Cont'd)

Preliminary Results of Overall Cost & Performance

	ZMR-IGCC	DOE Case 2 (Nexant Aspen)
Net plant efficiency	30.7%	31.5%
COE (mills/kWh)	138.1	138.6
Cost of CO_2 Avoided Excl CO_2 TS&M \$/Ton CO_2	56.0	54.8

Preliminary calculations were based on results of simplified ZMR reactor model:

- CO conversion: ~80% (~ 100%)
- H_2/H_2O selectivity: ~ 3/1 (~ 100/1)

Summary of Accomplishments, Training and Professional Development

. Milestone Status Report for Budget Period 1

ID	Task	Description	Planned Completion	Actual Completion	Verification Method
A	1	Updated Project Management Plan	2/29/2016	2/9/2016	Project Management Plan
B	1	Kick-off Meeting	1/31/2016	1/22/2016	Presentation file
C	1	Executed NCCC host site agreement	9/30/2016	4/17/2017	NCCC host site agreement
D	5	Fabrication of 25 cm long zeolite membrane tube with H_2/CO_2 selectivity >45 and H_2 permeance >600 GPU	9/30/2016	3/31/2017	Results reported in the quarterly report
E	2.3	Completion of WGS experiments in single-tube zeolite membrane reactor at pressures above 15 atm with simulated syngas	12/31/2016	12/31/2016	Results reported in the quarterly report

. Milestone Status Report for Budget Period 1 (Cont'd)

F	6.2	Fabrication procedures are established and 30 zeolite membrane tubes are prepared with H_2/CO_2 selectivity >45 and H_2 permeance >600 GPU exhibited	6/30/2017	6/30/2017*	Results reported in the quarterly report
G	8.2	Fabrication and successfully test performance of WGS in the intermediate-scale (7-14 tube bundles) membrane reactor with simulated syngas	6/30/2017	6/31/2017*	Results reported in the quarterly report
QR	1	Quarterly report	Each quarter	Quarterly Reports 1-6 submitted on time	Quarterly Report files

* anticipated completion dates.

Success Criteria at Decision Point

Decision Point	Basis for Decision/Success Criteria	Current Status
Completion of Budget Period 1	Successful completion of all work proposed in Budget Period 1.	On track for June 30, 2017
	Fabrication of 25 cm long zeolite membrane tube with H_2/CO_2 selectivity >45 and H_2 permeance >600 GPU	Success in synthesizing zeolite membranes having H_2/CO_2 selectivity >45, H_2 permeance >600 GPU Success in fabricating 7-tube intermediate scale bundles and module
	Success in testing WGS in 7 to 14-tube intermediate scale WGS zeolite membrane module with membranes having H_2/CO_2 selectivity >45, H_2 permeance >600 GPU and operational at feed pressure up to 30 bar in 400-550°C	Success in testing WGS in single-tube zeolite membrane reactor with membranes having H_2/CO_2 selectivity >40, H_2 permeance >300 GPU at feed pressure higher than 30 bar in 400-550°C; Testing of 7-tube intermediate scale WGS zeolite membrane module is in progress and expected to complete by June 30, 2017.
	Intermediate-scale WGS membrane reactor achieves CO conversion >99%, CO_2 capture/recovery >90% and CO_2 purity >95%	WGS membrane reactor achieves CO conversion >99%, CO_2 capture/recovery >90% and CO_2 purity >95%
	Submission and approval of a Continuation Application in accordance with the terms and conditions of the award.	Submitted April 25, 2017

Project Management

- Research teams had regular teleconferences (frequency ranging from biweekly to 2 monthly). We also had on-site meetings twice.
- The two university teams have recruited 1 post-doctor and 4 Ph.D. students to work on this project.
- These researchers have gained good skills and become highly capable, and are well positioned for more productive work on this project during BP 2.
- All quarterly and topical reports were submitted on time.

Summary of Expenses for Budget Period 1

	Budgeted amount for BP1		Expected Expenses by June 30, 2017	
	DOE	Cost-share	DOE	Cost-share
ASU	427,357	108,380	395,509	120,051
UC	339,002	85,860	355,850	94,971
MPT	371,678	92,920	354,560	88,640
Nexant	136,831	34,207	136,831	34,208
Total	1,274,868	321,367	1,242,750	337,870

- **DOE Fund, about 3% carry-over, mainly by MPT.**
- **Cost-share: 21.4% of the total expenses**

Plan for the work in the Current Quarter in BP1

Final Quarter of BP1 – Complete the Remaining Tasks for Budget Period 1

- ASU - continuing experiments on WGS in lab-scale ZMR to obtain parameters for modeling and TEA.

- UC – further improving synthesis of multiple zeolite membrane tubes in one batch, and preparing more zeolite membrane tubes for MPT and ASU.

- MPT - making 7-tube intermediate scale zeolite membrane bundles and membrane reactor modules, and testing their performance with synthetic syngas mixture under the conditions of WGS reaction at the MPT site.

- MPT - working with NCCC on technical and safety issues for design and modification of the membrane testing skid for testing the intermediate-scale zeolite membrane reactor

Plan for Budget Period 2 Work

- Discussion on Budget Period 2 Work
- Tasks and Timeline of BP2

Modification of Bench Scale Zeolite Membrane Reactor

- Zeolite membranes with H_2/CO_2 selectivity of about 40 and H_2 permeance >300 are sufficient to achieve desired CO conversion, H_2 recovery at high feed pressure (>20 bar)

Results of experimental WGS reaction tests in tubular zoelite membrane reactor

P_{cat} / bar	GHSV / h^{-1}	X_{CO} / %[2]		R_{H2} / %[3]		Reaction duration / h
		Exp.	Cal[4]	Exp.	Cal	
23.5	15000	~100	99.9	~100	99.9	38
26.5	30000	~100	99.9	~100	99.9	22

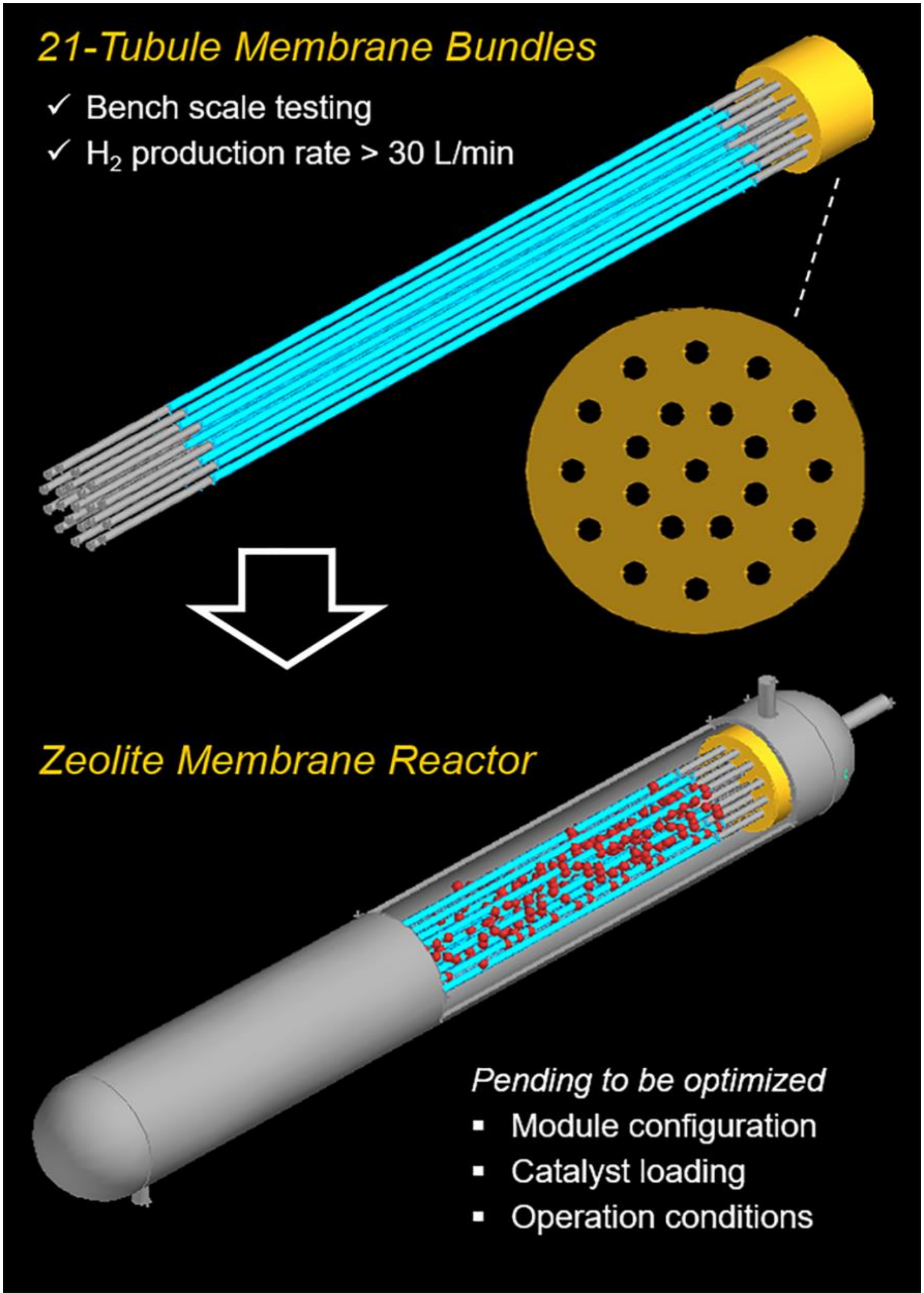
Membrane and WGS-Reactor Testing at NCCC

Composition and conditions of syngas at NCCC Site

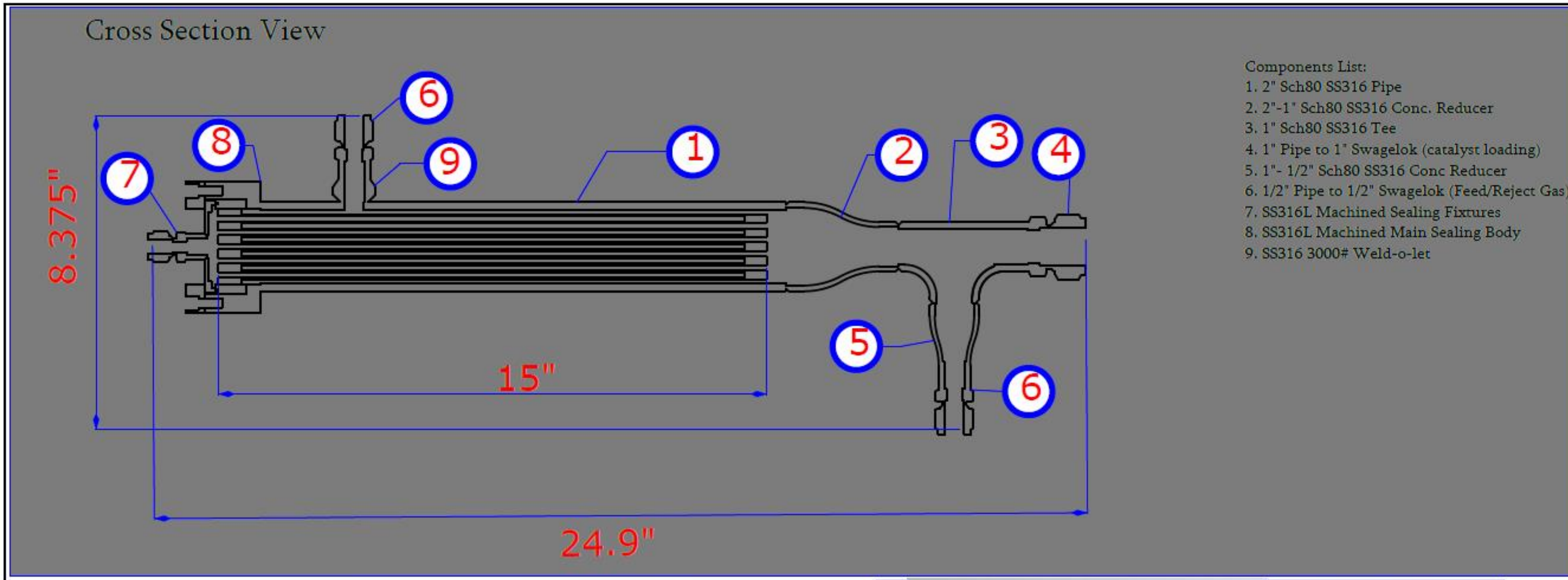
Composition or Temperature and pressure	NCCC Raw Syngas	Desired syngas for this project
H_2	5-7%	26%
CO	9-11%	27%
CO_2	9-11%	14%
N_2	69-74%	0
CH_4	0.9-1.2%	0
H_2O	~0	34%
H_2S	400 ppm	50 ppm (0.56%)[#]
Pressure	180-190 psig	285 psig (20 bar)
Temperature	500-550 F	350-550^{o}C

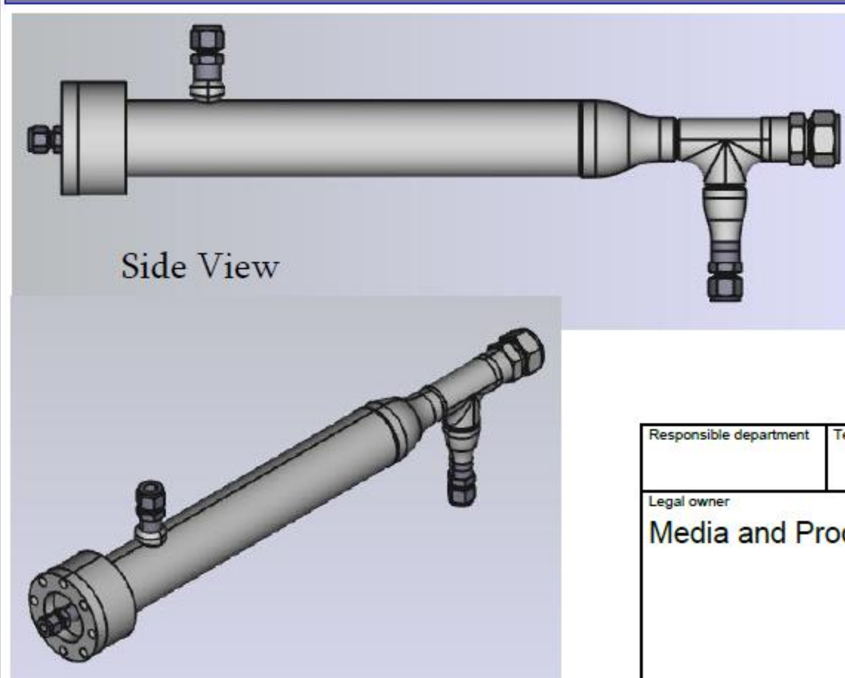
Bench-Scale Zeolite Membrane Reactors

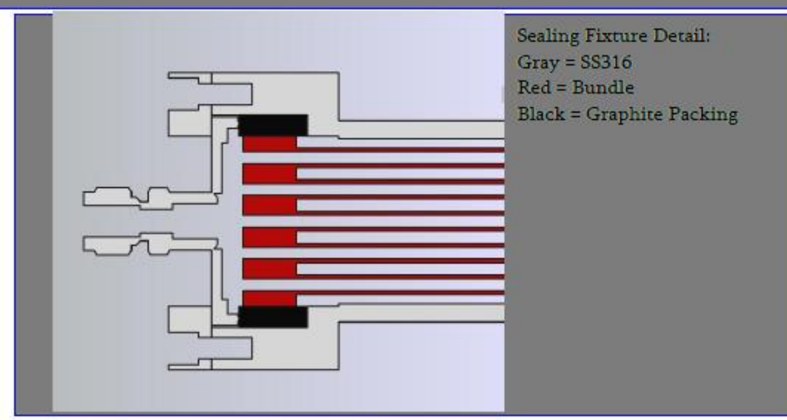
21 Tube, H_2 Production Rate 1-10 kg/Day



MPT's 21-Tube Bench-Scale Zeolite Membrane Reactor Design



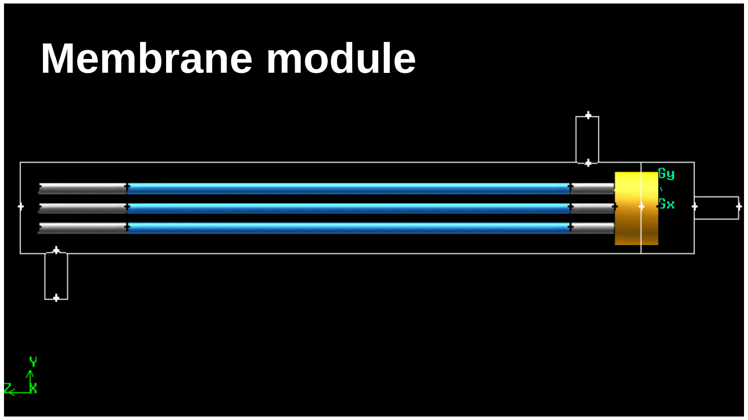


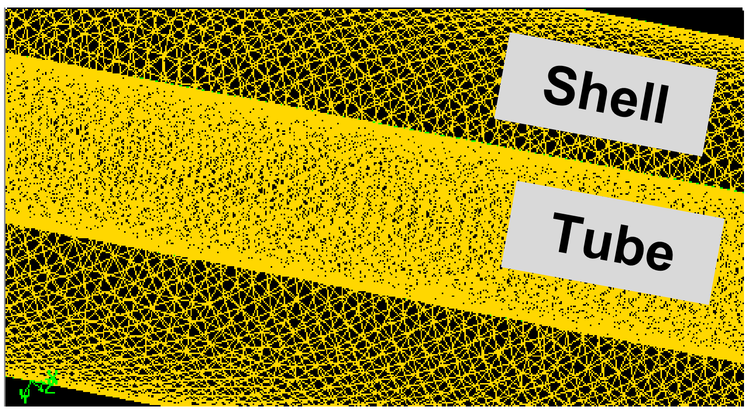


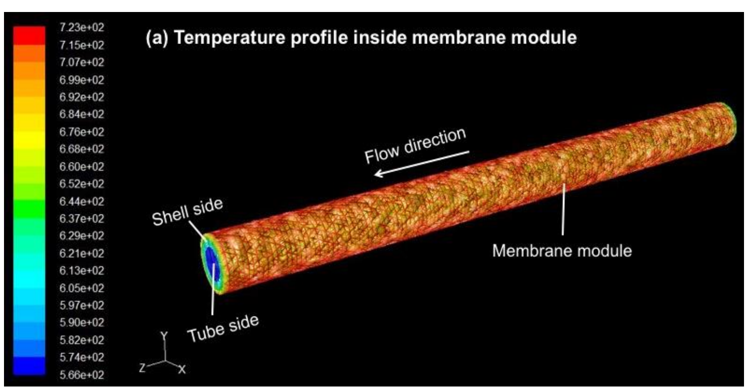
Responsible department	Technical reference	Created by: Doug P	Approved by: pending	Classification/key words
Legal owner: Media and Process Tech		Document type: initial mockup-review	Document status: initial review	
		Title, Supplementary title: 21 Tube ASU Bundle Housing	Identification number: 0001	
			Rev. / Date of issue: 2017-05-15	Language / Seg./Sh.

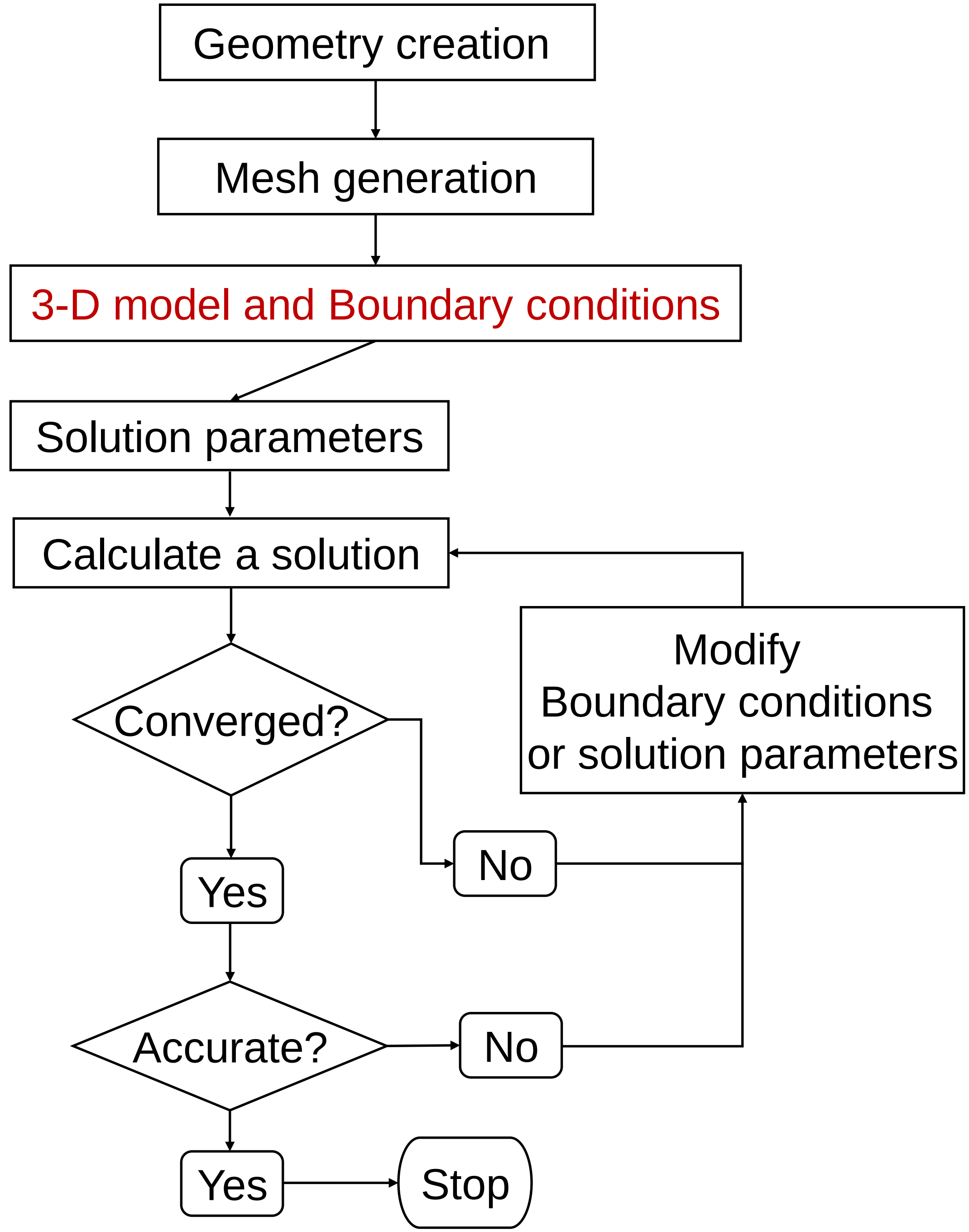
Modeling of 21 Tube Bench-Scale ZMR: 3-D CFD Simulation Approach

Software: *ANSYS Fluent*









Modeling of 21 Tube Bench-Scale ZMR: 3-D CFD Simulation Approach

Governing equations

Momentum transport (Navier-Stokes equation):

$$\nabla\cdot\left(\varepsilon\rho\overrightarrow{V}\right)=0$$

$$\frac{1}{\varepsilon^2}\nabla\cdot\left(\rho\overrightarrow{V}\overrightarrow{V}\right)=\nabla\cdot\left[-p\overleftrightarrow{I}+\frac{\mu_g}{\varepsilon}\left(\nabla\overrightarrow{V}+\left(\nabla\overrightarrow{V}\right)^T\right)-\frac{2\mu_g}{3}\overleftrightarrow{I}\nabla\cdot\overrightarrow{V}\right]+S_U$$

Energy transport:

$$\nabla\cdot\left(\varepsilon\rho c_p\overrightarrow{V}T\right)=\nabla\cdot\left(\lambda_e\nabla T\right)+q_c$$

Species transport:

$$\nabla\cdot\left\{\rho\overrightarrow{V}m_i-\rho m_i\sum_{j=1}^{N_G}\left[D_{ij,e}\left(\nabla x_i+\left(x_i-m_i\right)\frac{\nabla p}{p}\right)-D_i^T\frac{\nabla T}{T}\right]\right\}=r_i$$

WGS reaction rate equation

$$R=0.008\pm0.0004\exp\left(\frac{-60.3\pm1.3}{R'T}\right)P_{CO}^{0.75\pm0.12}P_{H_2O}^{0.31\pm0.08}P_{CO_2}^{-0.07\pm0.02}P_{H_2}^{-0.09\pm0.02}(1-\beta)$$

$$\beta=1/K\cdot P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$$

Gas permeation equation

$$j_i=\frac{\varphi}{\delta}\frac{\alpha}{\lambda}\left(\frac{8}{\pi RTM_i}\right)^{1/2}\exp\left(\frac{-E_{d,i}}{RT}\right)$$

Boundary conditions

Parameters for simulation		Provided by
Operation conditions:	Temperature, Pressure, Flow rate, and Gas composition.	ASU
Membrane characteristics:	Dimensions, Gas permeance, and Selectivity.	UC
Module design:	Dimensions, Cross-section layout and Materials.	MPT

BP2 Tasks and Project Timeline

Task	BP 2					
	Q4	Q1	Q2	Q3	Q4	Q1
Task 10.0 Modeling and Analysis of WGS in Bench Scale Zeolite Membrane Modules for WGS (ASU)						
Subtask 10.1 Modeling and analysis of WGS in multi-tube membrane reactor module						
Subtask 10.2 Optimization of operation conditions for WGS in zeolite membrane module						
Task 11.0. Fabrication of Large Quality Tubular Supports (MPT)						
Task 12.0 Preparation of Large Quantity MFI Zeolite Tube Membranes for Bench-Scale Module (UC)						
Subtask 12.1 Identifying conditions for fabrication of large quantity of zeolite membrane tubes						
Subtask 12.2 Fabrication of 100 zeolite membrane tubules with desired quality						
Task 13.0 Design and Fabrication of Bench-Scale Zeolite Membrane Module Housing with Seals (MPT/UC/ASU)						
Task 14.0 Building Bench-Scale Zeolite Membrane Reactors (MPT/ASU/UC)						
Subtask 14.1 Fabrication and evaluation of WGS catalyst for bench-scale WGS reaction (ASU)						
Subtask 14.2 Assembling and testing bench-scale zeolite membrane reactor (MPT/UC/ASU)						
Subtask 14.3. Modification and installation of the membrane reactor testing skid (MPT/ASU)						
Task 15.0 Testing WGS in Bench-Scale Membrane Reactor (MPT)						
Task 16.0 Process Design, Techno-Economic and EH&S Analyses (MPT)						
Subtask 16.1 Design of Commercial Scale WGS Zeolite Membrane Reactor and Process (MPT/Nexant)						
Subtask 16.2 Techno-Economic Analysis (TEA) of IGCC Plant (Nexant)						
Subtask 16.3 Preliminary Technology EH & S Assessment (MPT)						

Budget Period 2 Milestone Log

ID	Task	Description	Planned Comple-tion	Verification Method
H	11	Complete fabrication and characterization of at least 100 support tubules with nominal dimensions of 3.5 mm ID, 5.7 mm OD, and 35 cm length	12/31/2017	Results reported in the quarterly report
I	12	The bench-scale testing system with 21 zeolite tubes and WGS catalyst packed is ready for actual syngas operation at the NCCC host site	9/30/2018	Results reported in the quarterly report
J	15	Complete testing WGS in bench-scale zeolite membrane reactor with CO conversion >99%, H_2 recovery >92%, CO_2 capture >90% and CO_2 purity >95%	12/31/2018	Results reported in the quarterly report
K	16	Complete design of commercial zeolite membrane reactor as well as TEA and EH&S risk assessment of its integration with 550 MW IGCC plant	12/31/2018	Results reported in Topical Reports and Final Report
QR	1	Quarterly reports	Each quarter	Quarterly Report files
FR	1	Draft final report	1/31/2019	Draft Final Report file

Project Funding Profile for Budget Period 2

	Budget Period 2 (07/01/17-12/31/18)	
	Government Share	Cost Share
Arizona State University	$421,782	$101,607
University of Cincinnati	$339,988	$88,824
MPT Inc.	$371,750	$92,938
Nexant	$63,169	$15,792
Total	$1,196,689	$299,161
Cost Share	80%	20%

Success Criteria at Decision Point

Decision Point	Basis for Decision/Success Criteria
Completion of Budget Period 2	Successfully complete all work proposed in Budget Period 2.
	Complete fabrication of 21 zeolite membrane tubes with H_2/CO_2 selectivity >45 and H_2 permeance >600 GPU.
	Bench-scale zeolite membrane reactor system will be operated continuously for 300 hours during 500-hour gasifier run.
	Complete testing WGS in bench-scale zeolite membrane reactor with CO conversion >99.5%, H_2 recovery >99%, single stage CO_2 capture from membrane retentate >70% with CO_2 purity >99%.
	Achieve an increase in the net plant efficiency by at least 1% as compared to the DOE's Case 2 reference IGCC design with CO_2 capture (DOE/NETL 2010/1397 Report) with applying ZMRs to IGCC process in Techno-Economic Analysis.
	Submission of final report.


THANK YOU
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Palm
Walk